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Industrial Environmental Research Lab., Research Triangle Park, NC

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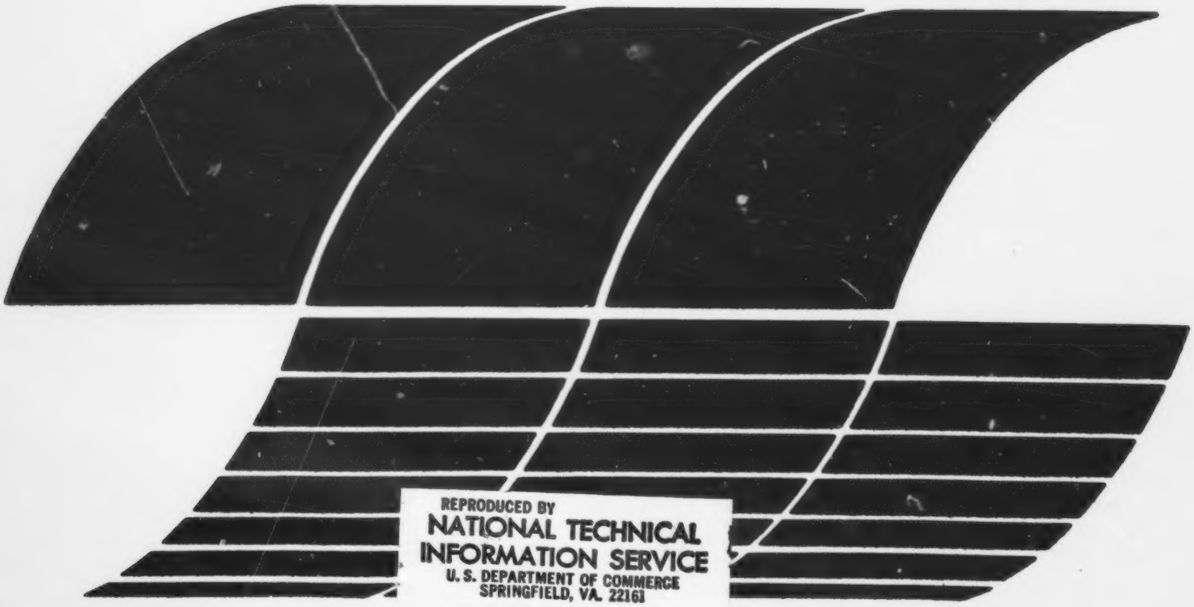

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16. ABSTRACT

The proceedings document presentations made at the Symposium on Coal Cleaning to Achieve Energy and Environmental Goals, September 11-15, 1978, in Hollywood, Florida. The symposium provided an opportunity for mutual review and discussion of: the physical and chemical coal cleaning programs of EPA, DoE, the Electric Power Research Institute, and numerous industrial organizations; European and Soviet plans for the future; and problems of ongoing operations. The proceedings include the following topics: coal characteristics, coal cleaning overview, physical coal cleaning technology, environmental assessment and pollution control technology, and chemical coal cleaning technology. The first three topics are covered in Volume I; the last two, in Volume II.

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Proceedings: Symposium on Coal Cleaning to Achieve Energy and Environmental Goals
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by

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ABSTRACT

The Symposium on Coal Cleaning to Achieve Energy and Environmental Goals was sponsored by the U.S. EPA's Industrial Environmental Research Laboratory under Contract No. 68-02-2163, Task No. 861. The Symposium was held September 11-15, 1978, in Hollywood, Florida. The program provided an opportunity for mutual review and discussion of the physical and chemical coal cleaning programs of EPA, DoE, the Electric Power Research Institute, those of numerous industrial organizations, and European and Soviet plans for the future, as well as the problems of ongoing operations.

The Proceedings contain the contributions of the participating speakers and include the following topics:

(a) Coal Characteristics
(b) Coal Cleaning Overview
(c) Physical Coal Cleaning Technology
(d) Environmental Assessment and Pollution Control Technology
(e) Chemical Coal Cleaning Technology.

FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise, industrial effluents, and other forms of pollution, as well as the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay among the components of our physical and biological environment--air, water, land, plants, and animals. The Industrial Environmental Research Laboratory (IERL/RTP) of the U.S. Environmental Protection Agency (EPA) located at Research Triangle Park, North Carolina, contributes to this multidisciplinary focus through programs engaged in:

- studies on the effects of environmental contaminants on the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This Symposium Proceedings deals with the subject matter of concern to an IERL/RTP program designed to focus on the effectiveness and efficiency of coal cleaning processes as a means of reducing the total environmental impact of energy production through coal utilization. The Symposium itself provided a most vital communication link between the researcher and engineer on the one hand and the user community on the other. To enhance future communication processes and encourage future applications of coal cleaning technology, this Symposium Proceedings documents the results of the meeting held.

ACKNOWLEDGMENT

No symposium can be a success without the support and participation of the attendees. For those participants listed elsewhere in this document, then, we are grateful for their contributions. Thanks in full measure is due also to the Session Chairmen and Cochairmen who patiently labored to formulate an informative and timely program. And, of course, none of this would have been possible without the long hours spent by the authors individually and collectively, in the preparation of their papers.

Thanks are also due for the handling of the mechanical details of the Symposium. These necessary functions were performed ably by a number of people. Mr. Jack H. Greene (IERL/RTP) was responsible for the overall arrangements with the hotel, and Ms. Susan R. Armstrong, Conference Coordinator at Battelle's Columbus Laboratories (BCL), managed the day-to-day activities. She was assisted in the many details of the necessary operations by Ms. Joyce B. Fowler (IERL/RTP), Mrs. Rebecca S. Miller (BCL), and Mrs. Lucy G. Pierson (BCL).

Special thanks are expressed to Mrs. Alexis W. Lemmon, Jr., and Mrs. L. David Tamny for their efforts in making the week more pleasant for the distaff accompaniers of the Symposium participants.

In the preparation of the printed Symposium Proceedings, Ms. Sharron E. Rogers performed excellently as Technical Editor. Mrs. Miller and Mrs. Pierson organized, formatted, and provided the necessary typing. We are grateful for their assistance.

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The Coal Cleaning Program
# of the Fuel Process Branch
OF EPA's IERL-RTP

T. Kelly Janes
Chief, Fuel Process Branch
Industrial Environmental Research
Laboratory-RTP
U.S. Environmental Protection Agency
Research Triangle Park, N. C.

EPA's Industrial Environmental Research Laboratory at Research Triangle Park, N.C., conducts a contractual and in-house research, development, and demonstration program dealing with the control of emissions/discharges from energy related technologies and industrial processes.

The Laboratory is divided into three technical divisions:

1. Utilities and Industrial Power Division which primarily addresses the emissions controls for the combustion of fossil fuels to generate steam and electrical power.
2. Energy Assessment and Control Division which develops improved combustion techniques for nitrogen oxide control, advanced combustion systems, and the environmental effects and control techniques for coal processing and conversion of coal to synthetic liquids and gases.
3. Industrial Processes Division which addresses the emission and controls from industrial operations. Additionally, in this Division, analytical and sampling techniques are developed.

The Fuel Process Branch in the Energy Assessment and Control Division conducts programs addressing two major areas:

1. Coal Cleaning. Development of physical and chemical techniques to remove contaminants from coal; assessment of the environmental consequences from the utilization of coal cleaning processes; and the development of control technology to avoid adverse discharge effects.
2. Synthetic Fuels. The assessment of the multimedia discharges and control technique evaluation for technologies converting coal to gaseous, liquid, and refined solid fuels.

Both programs deal with the multimedia (air, water, and solid) discharge effects. However, the coal cleaning program has the additional responsibility to develop the basic processing technology. In 1965, EPA (and its prior organizations) initiated studies to determine the applicability of physical coal cleaning to reduce emissions from the combustion of coal. Early in this program it was apparent that additional information would be required before the assessment of this technology could be made. Thus, numerous projects were initiated to:

1. Evaluate the degree of pyrite removal which could be obtained from cleaning of U.S. coals.

2. Determine the effectiveness of commercial coal preparation techniques to maximize pyrite separation.

3. Evaluate processes that could utilize the coal reject mineral matter to aid in offsetting the increased cost of coal cleaning.

Since then, the coal cleaning program has passed through three major phases.

Phase I. The development of data and information which would provide a data base to assess the applicability of coal cleaning to maximize sulfur reduction. Technical areas addressed during this phase were:

- Laboratory evaluation of potential pyrite ash removal as affected by size reduction and specific gravity.

- Mineral constituents of U.S. coals.

- Applicability and effectiveness of existing coal cleaning techniques to maximize pyrite separation and removal.

- Available technology for recovery of economic values from coal cleaning refuse.

- Quality and quantity of U.S. coal reserves.

- Investigation and development of new or modified physical cleaning techniques for removal of pyrite and other contaminants from coal.

- Design of a coal cleaning pilot plant to evaluate cleanability of coals and performance of cleaning equipment.

Phase II. In the late 1960s, it became quite apparent that improved cleaning techniques would be necessary to increase sulfur removal to meet future requirements. These methods would need to be basically unaffected by pyrite size variations which have a marked effect on physical separation methods. Thus, a broad evaluation of various chemical cleaning techniques was conducted. Some 24 chemical reagents were evaluated for sulfur removal potential. The results showed that organic sulfur removal was extremely difficult and that the inorganic sulfur removal potential was much closer to realization. Thus, the ferrous sulfate leaching process development was initiated and carried through reactor pilot evaluation. Additionally, evaluations of other techniques, using hydrogen and microwave energy, were supported. The potential effectiveness of organic sulfur removal may well depend on prior removal of pyrite and other inorganic material.

Phase III. In the early 1970s, natural gas and oil shortages became a public concern and the need to fully utilize the nation's vast coal reserves became a federal goal. This concern with energy and increased use of coal was accompanied by a parallel concern with the potential impact that increased coal utilization would have on the health and ecological systems of the nation. This phase of the EPA coal cleaning program is concentrating on the identification of environmental impacts of discharges by using both chemical and biological evaluations.

The ongoing program covers a wide spectrum of activities from coal contaminant variability through evaluation of effects that clean coal will have on existing controls for combustion waste gas.

During this symposium, details of these ongoing efforts will be dealt with.

The reports listed on the following pages were prepared under the sponsorship and direction of IERL-RTP. For convenience these reports are listed under the following categories: coal characterization, evaluation of coal cleaning techniques, coal reject treatments, coal cleaning prototype plant, chemical coal cleaning, and applicability studies.

EPA/IERL-RTP REPORTS

Contractor (Contract No.)	NTIS No. (EPA No.)	Report Title -- Date Published(No. of Pages)
Coal Characterization		
Illinois State Geological Survey (PH 86-67-206)	PB 206-464 (APTD 0915)	Sulfur varieties in Illinois coals float sink tests (final phase I) -- 8/69 (98 pp)
	PB 205-952 (APTD 0841)	Sulfur reduction of Illinois coal washability studies (final phase II) -- 8/69 (98 pp)
U.S. Bureau of Mines	RI 7633 (APTD 1365)	Sulfur reduction potential of the coals of the U.S. -- 1972 (304 pp)
U.S. Bureau of Mines	RI 7608	Washability examinations of core samples of San Juan Basin coals, New Mexico and Colorado -- 1972 (30 pp)
Exxon (68-02-0629)	PB 225-039/7AS EPA-R2-73-249	Potential pollutants in fossil fuels -- 6/73 (293 pp)
Illinois State Geological Survey (68-02-0246)	PB 238-091/AS EPA-650/2-74-054	Occurrence and distribution of potentially volatile trace elements in coal -- 7/74 (106 pp)
U.S. Bureau of Mines (IAG-P5-0685)	PB 252-965/AS EPA-600/2-76-091	Sulfur reduction potential of U.S. coals: a revised report of investigations -- 4/76 (329 pp)
Los Alamos Scien. Lab (IAG-D5-E681)	PB 267-339/AS EPA-600/7-76-007	Environmental contamination from trace elements in coal preparation wastes -- 8/76 (69 pp)
Illinois State Geological Survey (68-02-1472)	PB 270-922/AS EPA-600/7-77-064	Trace Elements in Coal: occurrence and distribution -- 6/77 (165 pp)
Los Alamos Scien. Lab (IAG-D5-E681)	LA-6835-PR EPA-600/7-78-028	Trace element characterization of coal wastes - first annual report -- 3/78 (58 pp)
U.S. Dept. of Energy (IAG DXE685-AJ)	PB 280-759/AS EPA-600/7-78-038	Washability and analytical evaluation of potential pollution from trace elements in coal -- 3/78 (41 pp)

EPA/IERL-RTP REPORTS (cont)

Contractor (Contract No.)	NTIS No. (EPA No.)	Report Title -- Date Published(No. of Pages)
Evaluation of Coal Cleaning Techniques		
Bituminous Coal Research (PH 86-67-139)	PB 193-486 (APTIC 23423)	An evaluation of coal cleaning processes and techniques for removing pyritic sulfur from fine coal (interim report) -- 9/69 (285 pp)
	PB 193-484/ 193-532 (APTD 0579)	Same. Final report -- 2/70 (146 pp)
U.S. Bureau of Mines	RI 7440 (APTIC 31443)	Electrophoretic - specific gravity separation of pyrite from coal, laboratory study -- 10/70 (15 pp)
U.S. Bureau of Mines	RI 7518	Hydrolyzed metal ions as pyrite depressants in coal flotation: a laboratory study -- 5/71 (26 pp)
Bituminous Coal Research (CPA 70-26)	PB 205-185/ 199-484 (APTD 0842)	An evaluation of coal cleaning processes and techniques for removing pyritic sulfur from fine coal -- Final report - 4/71 (173 pp)
U.S. Bureau of Mines	RI 7623	Photoelectric concentrator for the wet concentrating table -- 1972 (10 pp)
U.S. Bureau Mines	TPR 51	Flotation of pyrite from coal -- 2/72 (9 pp)
Bituminous Coal Research (68-02-0024)	PB 210-821 (APTD 1160)	An evaluation of coal cleaning processes and techniques for removing pyritic sulfur from fine coal (final report) -- 4/72 (174 pp)
J.J. Davis (68-02-1834)	PB 262-716/AS EPA-600/2-76-138	Coal preparation environmental engineering manual -- 5/76 (729 pp)
Mitre (68-02-1352)	PB 232-011/AS EPA-650/2-74-030	An interpretative compilation of EPA studies related to coal quality and cleanability -- 5/74 (276 pp)
Coal Reject Treatments		
Bechtel (PH 86-67-224)	PB 182-358 (APTD 1266)	Process costs and economics of pyrite-coal utilization (final report, Phases 1 & 2) -- 12/68 (187 pp)
A. D. Little (PH 86-67-258)	PB 182-303 (APTD 1274)	A study of process costs and economics of pyrite-coal utilization (final report) -- 3/68 (265 pp)

EPA/IERL-RTP REPORTS (cont)

Contractor (Contract No.)	NTIS No. (EPA No.)	Report Title -- Date Published(No. of Pages)
Coal Reject Treatments (cont)		
Chemical Constr. (CPA 22-69-151)	PB 203-958 (APTD 0768)	High sulfur combustor study (Final report) Vol. I, narrative summary -- 2/71 (226 pp)
	PB 203-959 (APTD 0769)	Same. Vol. II, descriptive detail -- 2/71 (450 pp)
Coal Cleaning Prototype Plant		
McNally Pittsburgh (PH 22-68-59)	PB 196-631 (APTD 0606)	A study on design and cost analysis of a prototype coal cleaning plant, Parts 1-6 -- 7/69 (147 pp)
	PB 196-632 (APTD 0607)	Coal cleaning plant prototype plant specifications, Part 7 -- 7/69 (200 pp)
	PB 196-633 (APTD 0608)	Coal cleaning plant prototype plant design drawings, Part 8 - 7/69 (20 pp)
	PB 196-634 (APTD 0609)	Design and cost analysis of a prototype coal cleaning plant. Supplement -- 7/69 (13 pp)
Roberts/Schaefer (PH 22-68-62)	PB 220-700 (APTD 0605)	Design and cost analysis study for a prototype coal cleaning plant, Vol. I -- 8/69 (109 pp)
	PB 220-701 (APTD 0605)	Same. Vol. II -- 8/69 (211 pp)
Roberts/Schaefer (CPA 70-157)	(Not in NTIS) EPA-R2-73-154	Research program for the prototype coal cleaning plant - 1/73 (133 pp)
Chemical Coal Cleaning		
TRW (CPA 71-7)	PB 204-863 (APTD 0845)	Chemical removal of nitrogen and organic sulfur from coal (final report) -- 5/71 (60 pp)
	PB 221-405 EPA-R2-73-173a	Chemical desulfurization of coal: report of bench scale developments. Vol. I -- 2/73 (184 pp)
	PB 221-406 EPA-R2-73-173B	Same. Vol. II -- 2/73 (85 pp)

EPA/IERL-RTP REPORTS (cont.)

Contractor (Contract No.)	NTIS No. (EPA No.)	Report Title -- Date Published(No. of Pages)
Chemical Coal Cleaning (cont)		
TRW (68-02-0647)	PB 232-083/AS EPA-650/2-74-025	Applicability of the Meyers process for chemical desulfurization of coal: initial survey of fifteen coals -- 4/74 (200 pp)
	PB 254-461/AS EPA-650/2-74-025a	Same: survey of thirty-five coals -- 9/75 (212 pp)
Dow Chemical (68-02-1329)	PB 241-927/AS EPA-650/2-75-032a	Energy consumption: the chemical industry (task 5) -- 4/75 (71 pp)
Exxon (68-02-0629)	PB 246-311/AS EPA-650/2-74-009k	Evaluation of pollution control in fossil fuel conversion processes -- coal treatment; section 1: Meyers process -- 9/75 (46 pp)
TRW (68-02-1336)	PB 261-128/AS EPA-600/2-76-143a	Meyers process development for chemical desulfurization of coal, Vol. I -- 5/76 (309 pp)
	PB 261-129/AS EPA-600/2-76-143b	Same, Vol. II -- appendices -- 5/76 (124 pp)
TRW (68-02-1335)	PB 270-111/AS EPA-600/2-77-080	Pilot plant design for chemical desulfurization of coal -- 4/77 (162 pp)
Applicability Studies		
Mitre (F-192628-68C-0365)	PB 210-373 (APTD 0844)	The physical desulfurization of coal -- major considerations for SO_2 emission control -- 11/70 (340 pp)
	PB 197-386 (APTD 0627)	A survey of fuel and energy information sources, Vol. I -- 11/70 (307 pp)
	PB 197-387 (APTD 0628)	Same. Vol. II - 11/70 (632 pp)
Hittman Associates (EHSD 71-43)	PB 209-266 (APTD 1079)	Electric power supply and demand forecasts for the United States through 2050 -- 2/72 (54 pp)
Mitre (USAF 723)	PB 211-505 EPA-R2-72-022	Survey of coal availabilities by sulfur content -- 5/72 (168 pp)
M. W. Kellogg (68-02-1308)	PB 239-496/AS EPA-650/2-74-127	Evaluation of sulfur dioxide emission options for Iowa power boilers (task 3) -- 12/74 (331 pp)

EPA/IERL-RTP REPORTS (cont.)

Contractor (Contract No.)	NTIS No. (EPA No.)	Report Title -- Date Published(No. of Pages)
Applicability Studies (cont)		
Battelle (68-02-2112)	PB 256-020/AS EPA-600/2-76/177a	Fuel contaminants: Vol. 1, Chemistry -- 7/76 (177 pp)
	PB 260-475/AS EPA-600/2-76-177b	Same; Vol. 2, removal technology evaluation -- 9/76 (318 pp)
Battelle (68-02-2163)	PB 277-408/AS EPA-600/7-78-034	Physical coal cleaning for utility boiler SO_2 emission control (task 851) -- 2/78 (112 pp)

ENVIRONMENTAL ASSESSMENT METHODOLOGIES FOR FOSSIL ENERGY PROCESSES: AN UPDATE

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ABSTRACT

Industrial Environmental Research Laboratory, Research Triangle Park, (IERL/RTP) is conducting a number of programs involving environmental assessment and control technology for both energy and industrial processes. This presentation focuses on some aspects of the environmental assessment (EA) methodology being developed and used as it relates to the Federal Interagency Environmental R&D program.

A satisfactory environmental assessment methodology needs to address all program aspects such as air, water, solid waste, toxic substances, radiation, and noise. Essentially all pollutants and environmental factors should be addressed including chemical substances; heat; noise; microorganisms; radiation; and air-, water-, and land-related physical factors. Energy technologies selected for investigation should be those with high commercial usage/application potential. The methodology must be practical and therefore has to be based on utilization of available or readily obtainable information. Since absolute answers are not usually achievable, emphasis must be placed on comparative evaluations; e.g., definition of the relative best ways of controlling and relative comparison of waste streams and sources.

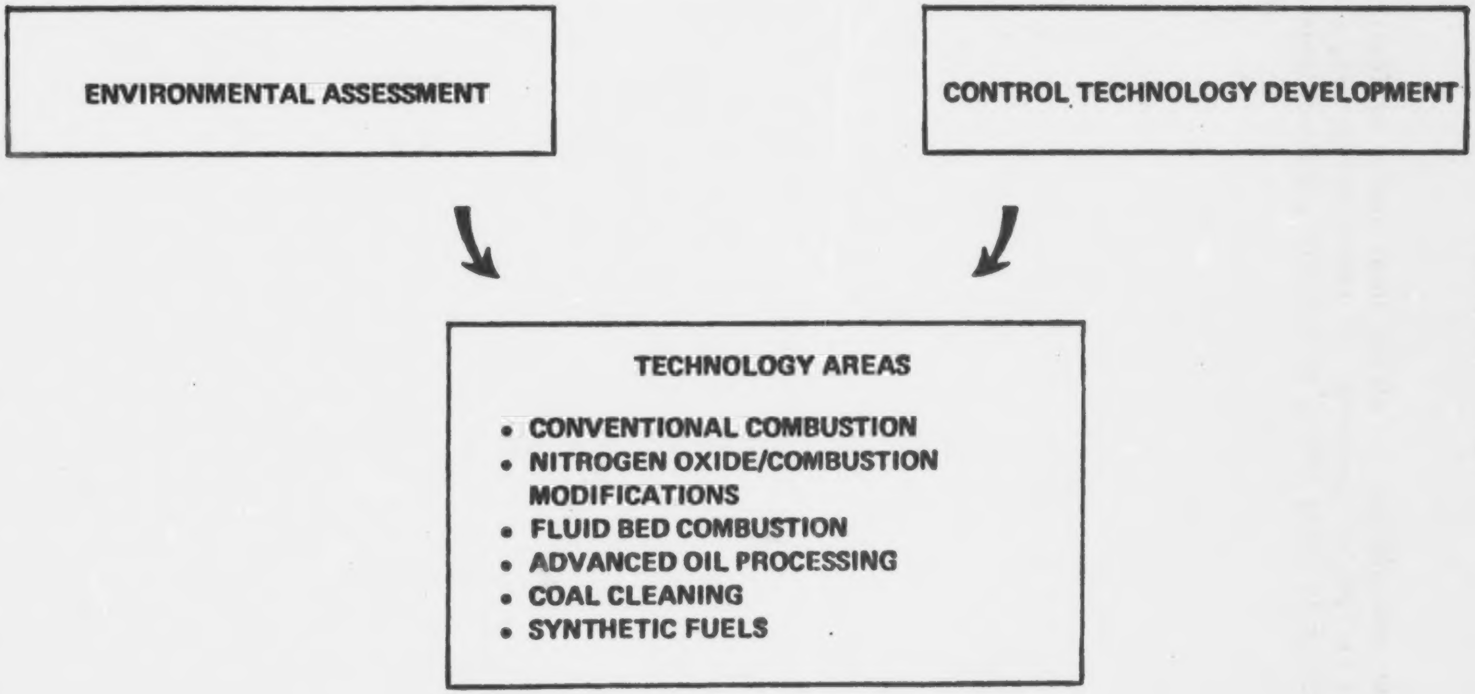
The methodology is evolving out of necessity and should employ cost-effective approaches to effect broad-coverage screening initially followed by detailed screening to focus on areas of concern. The approaches must be subject to continued refinement and improvement based on data and experience gained in doing EA studies. Long lead times must be dealt with in development and implementation of the methodology.

Several aspects of the developing environmental assessment methodology are discussed including the areas of current process technology background, environmental data acquisition, current environmental background, environmental objectives development, control technology assessment, and environmental alternatives analysis. Some of the barriers to implementation are noted also.

ACKNOWLEDGEMENTS

The author acknowledges the direct input and/or availability of information developed by IERL/RTP personnel and their contractors, and personnel of other laboratories in EPA's Office of Research and Development.

ENVIRONMENTAL ASSESSMENT AND CONTROL TECHNOLOGY DEVELOPMENT PROGRAM

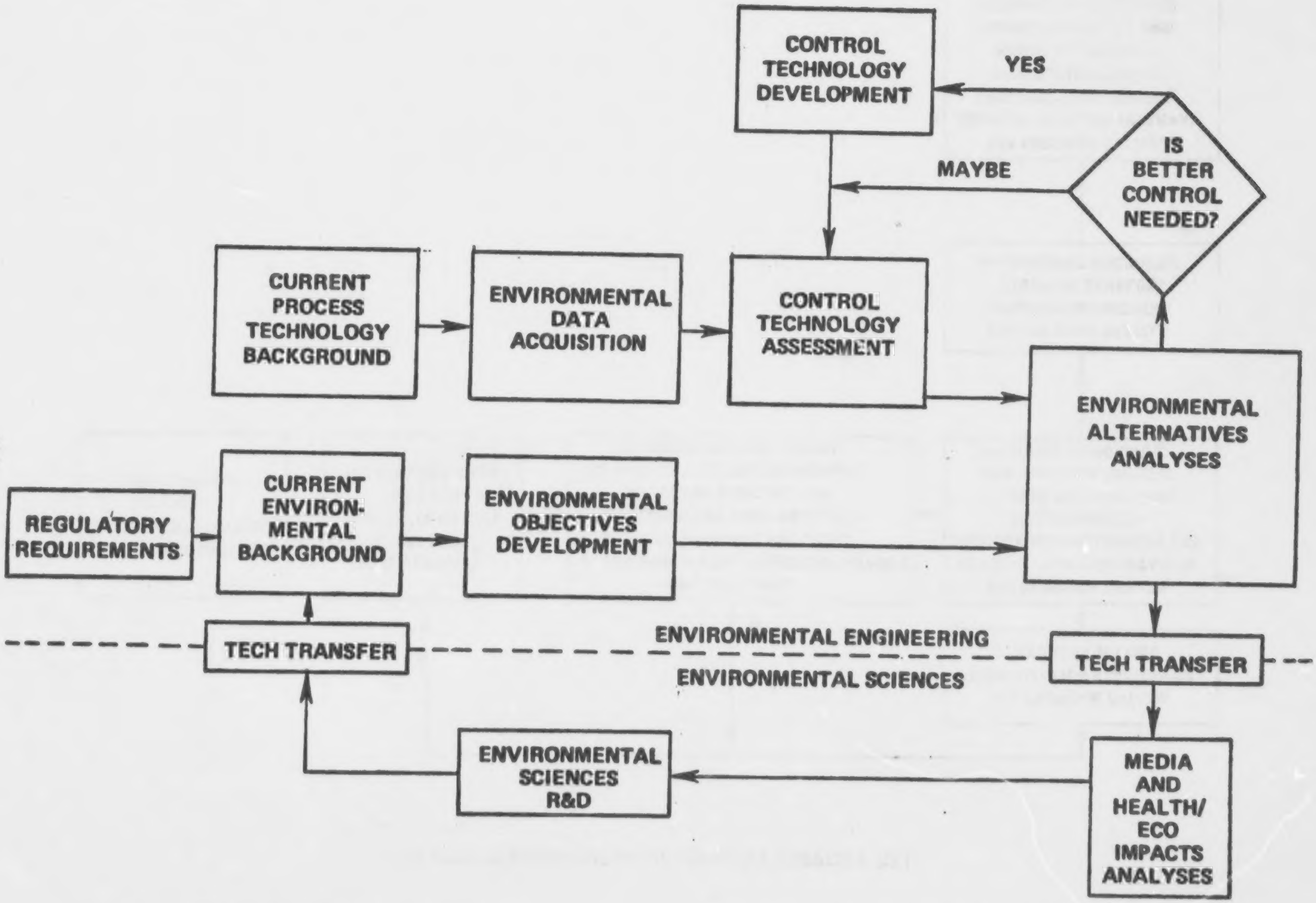


ENVIRONMENTAL ASSESSMENT

CONTROL TECHNOLOGY DEVELOPMENT

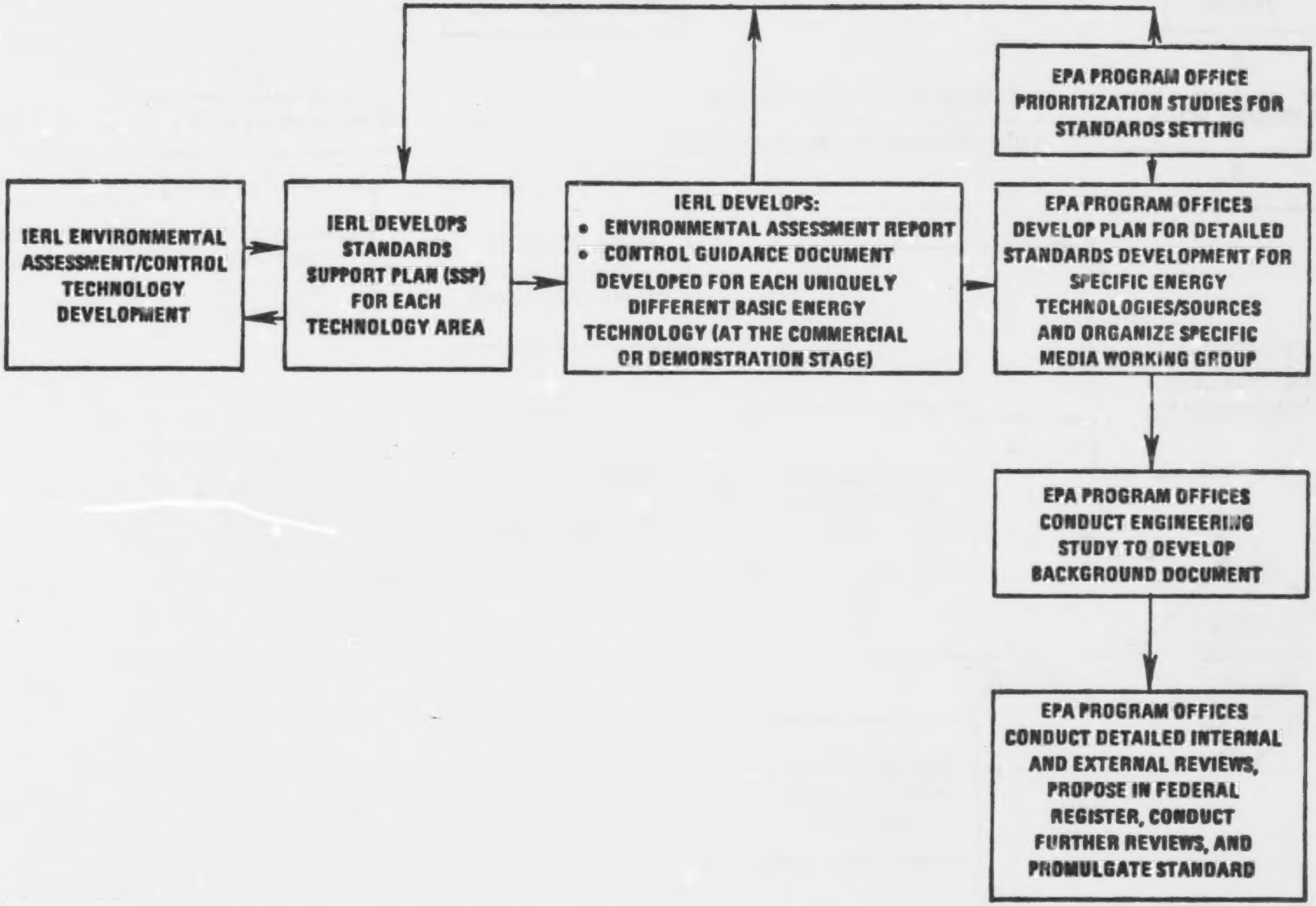
TECHNOLOGY AREAS

- CONVENTIONAL COMBUSTION
- NITROGEN OXIDE/COMBUSTION MODIFICATIONS
- FLUID BED COMBUSTION
- ADVANCED OIL PROCESSING
- COAL CLEANING
- SYNTHETIC FUELS


CONTROL TECHNOLOGY DEVELOPMENT
YES
MAYBE
IS BETTER CONTROL NEEDED?
CURRENT PROCESS TECHNOLOGY BACKGROUND
ENVIRONMENTAL DATA ACQUISITION
CONTROL TECHNOLOGY ASSESSMENT
ENVIRONMENTAL ALTERNATIVES ANALYSES
REGULATORY REQUIREMENTS
CURRENT ENVIRON-MENTAL BACKGROUND
ENVIRONMENTAL OBJECTIVES DEVELOPMENT
TECH TRANSFER
ENVIRONMENTAL ENGINEERING
ENVIRONMENTAL SCIENCES
TECH TRANSFER
ENVIRONMENTAL SCIENCES R&D
MEDIA AND HEALTH/ ECO IMPACTS ANALYSES

ENVIRONMENTAL ASSESSMENT/CONTROL TECHNOLOGY DEVELOPMENT DIAGRAM

IERL/RTP STANDARDS DEVELOPMENT SUPPORT R&D


IERL ENVIRONMENTAL ASSESSMENT/CONTROL TECHNOLOGY DEVELOPMENT
IERL DEVELOPS STANDARDS SUPPORT PLAN (SSP) FOR EACH TECHNOLOGY AREA
IERL DEVELOPS:
• ENVIRONMENTAL ASSESSMENT REPORT
• CONTROL GUIDANCE DOCUMENT
DEVELOPED FOR EACH UNIQUELY DIFFERENT BASIC ENERGY TECHNOLOGY (AT THE COMMERCIAL OR DEMONSTRATION STAGE)
EPA PROGRAM OFFICE PRIORITIZATION STUDIES FOR STANDARDS SETTING
EPA PROGRAM OFFICES DEVELOP PLAN FOR DETAILED STANDARDS DEVELOPMENT FOR SPECIFIC ENERGY TECHNOLOGIES/SOURCES AND ORGANIZE SPECIFIC MEDIA WORKING GROUP
EPA PROGRAM OFFICES CONDUCT ENGINEERING STUDY TO DEVELOP BACKGROUND DOCUMENT
EPA PROGRAM OFFICES CONDUCT DETAILED INTERNAL AND EXTERNAL REVIEWS, PROPOSE IN FEDERAL REGISTER, CONDUCT FURTHER REVIEWS, AND PROMULGATE STANDARD

BREADTH OF OBJECTIVES

- COMPREHENSIVE CONTROL GUIDANCE IS NEEDED ON REAL-TIME BASIS IN DEVELOPING, EVALUATING, AND DESIGNING CONTROL TECHNOLOGY.

- ALL MEDIA/PROGRAM OFFICES NEED TO BE ADDRESSED (AIR, WATER, SOLID WASTE, TOXIC SUBSTANCES, RADIATION, NOISE).

- ALL IMPORTANT POLLUTANTS AND ENVIRONMENTAL FACTORS SHOULD BE ADDRESSED (CHEMICAL SUBSTANCES; HEAT; NOISE; MICRO-ORGANISMS; RADIATION; AND AIR-, WATER-, AND LAND-RELATED PHYSICAL FACTORS).

- TECHNOLOGIES INVESTIGATED SHOULD HAVE HIGH COMMERCIAL USAGE/APPLICATION POTENTIAL.

- SUMMARY OF NEEDS FOR ADDITIONAL DATA TO SUPPORT STANDARDS DEVELOPMENT, ENFORCEMENT, HEALTH AND ECOLOGICAL EFFECTS RESEARCH, AND CONTROL TECHNOLOGY R&D.

EFFECTS OF SCALE ON EA APPROACH AND OUTPUTS

Scale of Technology Facility	Practical Environmental Measurements	Practical Use of Information from Environmental Measurements
Bench-Scale Facility	Effluent/Product Analyses	• Identify Potential Pollutants for EA Measurements
Scaleable Pilot or Demo Plant with Nonscaleable Control Technology	Effluent/Product Analyses	• Good Identification of Pollutants • Projected Hazard of Untreated Streams Including Relationship to Fugitive Emissions and Spills • Estimates of Ambient Loadings Using Estimates of Add-On Control Effectiveness
	Control Assays	• Basic Data for Design of Controls
Full-Scale Facility with Applicable Controls	Effluent/Product Analyses	• Accurate Control Technology Evaluations • Good Projections of Ambient Loadings and Effects
	Ambient Measurements and Field Surveys	• Actual Ambient Loadings and Effects

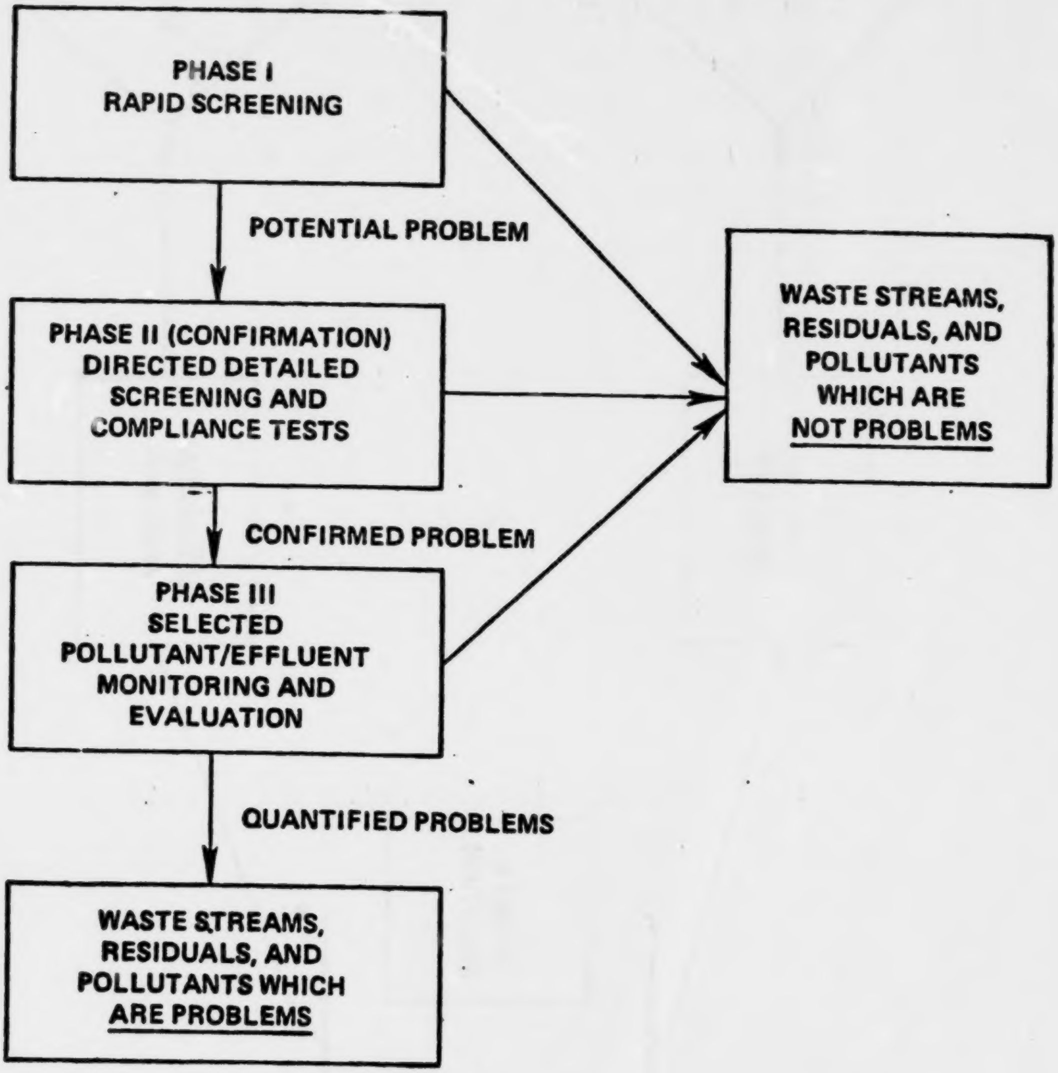
ENVIRONMENTAL DATA ACQUISITION
Level 1 Sampling and Analysis

EFFLUENT SAMPLES:	**GASES** **LIQUIDS** **SOLIDS**
EVALUATED FOR DISCHARGE TO MEDIA:	**AIR** **WATER** **LAND**
ANALYSES:	**PHYSICAL** **CHEMICAL** **BIOLOGICAL**
KEY ENVIRONMENTAL PARAMETERS:	**HEALTH** **ECOLOGICAL** **— FRESHWATER** **— MARINE** **— TERRESTRIAL**

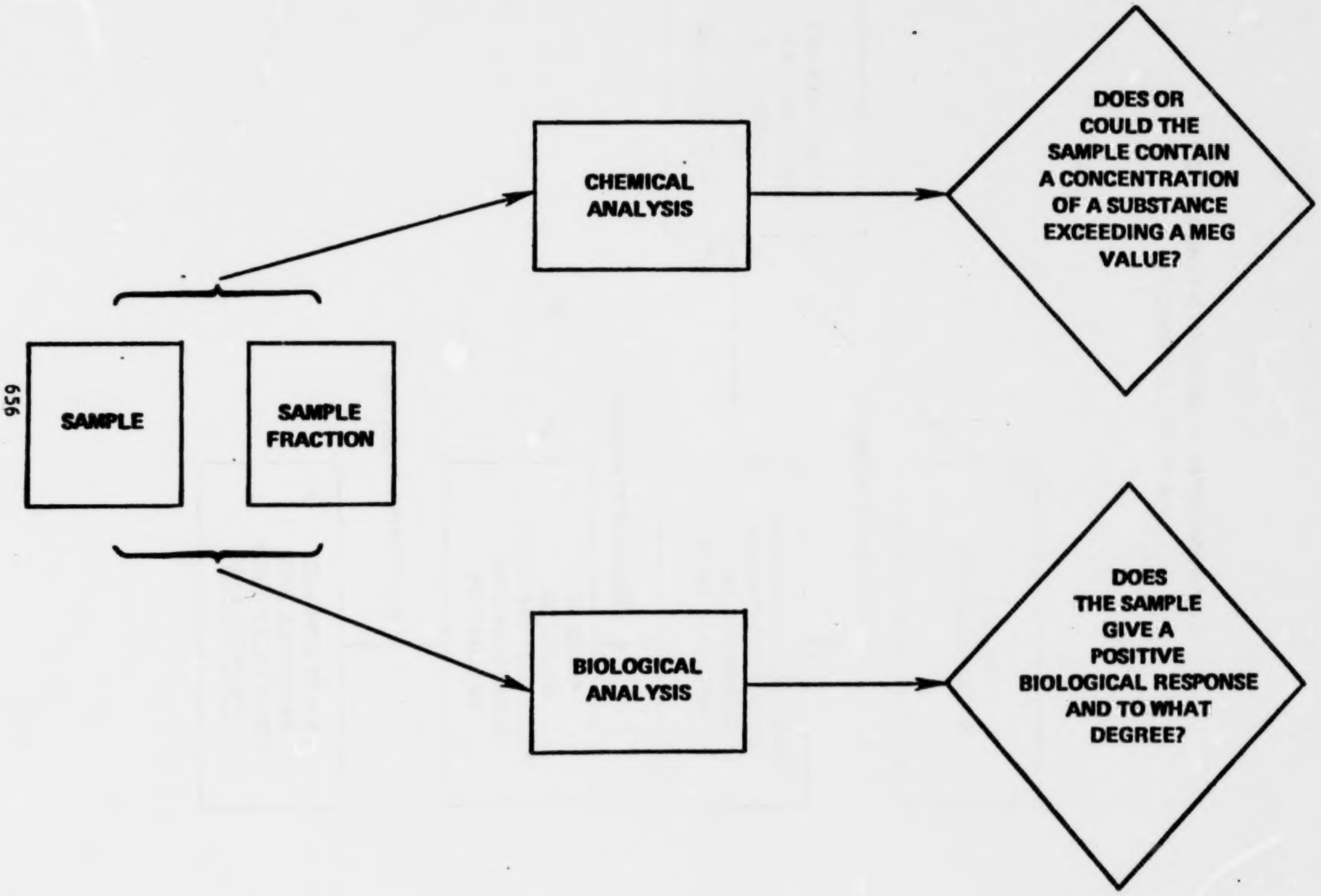
STATUS OF PHASED APPROACH TO CHEMICAL AND BIOLOGICAL ANALYSES

- LEVEL 1
  - PROCEDURES AVAILABLE
  - ADDITIONS AND REVISIONS UNDER STUDY
  - EVALUATION OF LEVEL 1 CHEMICAL AND BIOLOGICAL PILOT STUDIES NEAR COMPLETION FOR FLUID BED COMBUSTION, GASIFIER, AND TEXTILE PLANTS; RESULTS LOOK GOOD.
- LEVEL 2
  - GENERALIZED INTERIM PROCEDURES AVAILABLE FOR ORGANICS
  - GENERALIZED PROCEDURES FOR INORGANICS WILL BE AVAILABLE SOON
  - BASIC OUTLINE FOR LEVEL 2 BIOASSAY PROTOCOL WILL BE AVAILABLE LATER THIS YEAR
- LEVEL 3
  - GUIDELINES ARE NOT YET DEVELOPED--WILL BE SITE (PROCESS) SPECIFIC

ENVIRONMENTAL ASSESSMENT METHODOLOGY
— A PHASED APPROACH —



PARALLEL ANALYSIS APPROACH


SAMPLE
SAMPLE FRACTION
CHEMICAL ANALYSIS
BIOLOGICAL ANALYSIS
DOES OR COULD THE SAMPLE CONTAIN A CONCENTRATION OF A SUBSTANCE EXCEEDING A MEG VALUE?
DOES THE SAMPLE GIVE A POSITIVE BIOLOGICAL RESPONSE AND TO WHAT DEGREE?

REGULATORY APPROACHES AND POTENTIAL REQUIREMENTS

AIR (CAA)
- NSPS
- Guidelines/Documents
- PSD (BACT)
- Nonattainment (LAER)
- NESHAP
- Air Quality Criteria (inputs on sources and control technology documents)

WATER (FWPCA, SDWA)
- Effluent Guidelines
    - BPT (1977)
    - BAT (toxic pollutants - 1984)
    - BCCT (conventional pollutants - 1984)
    - BAT (all other pollutants - 1987)
- NSPS
- Toxic and Pretreatment Effluent Standards
- Permits
    - Ocean Discharge
    - SDWA (underground injection groundwater protection)
    - National Pollution Discharge Elimination System
    - Area-Wide Waste Treatment Management (State/208 agencies)
- Hazardous Materials (spills, etc.)
- Water Quality Standards and Criteria

SOLID WASTES (RCRA)
- Criteria, Identification Methods, and Listing of Hazardous Wastes
- Standards Application to Owners and Operators of Hazardous Waste Treatment, Storage and Disposal Facilities
    - Media Protection Strategies (groundwater, surface water, air)
- Guidelines

TOXIC SUBSTANCES (TOSCA)
- Implementation/Development
    - Listing
    - Prioritization
- Reporting Requirements
- Premature Notification
- Testing
- Control

RADIATION
- Guidance for Control (CAA, FWPCA, RCRA, TOSCA)

NOISE
- Data Base, if Regulated in Future
- Guidance

LAND USE
- Data Base, if Regulated in Future

CURRENT ENVIRONMENTAL BACKGROUND

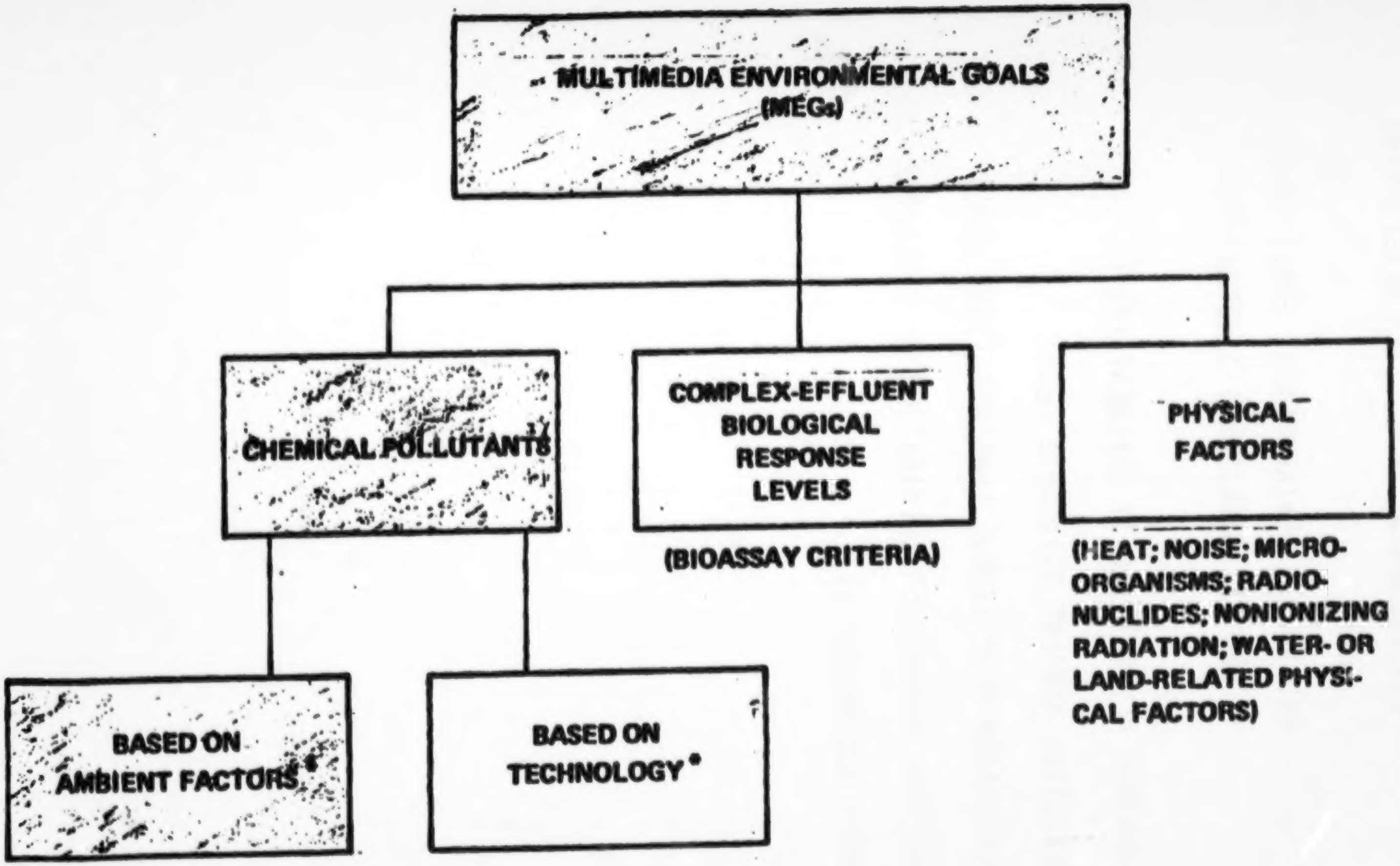
- Summary of Key Federal Regulations
- Noncriteria Ambient Baseline Data
- Environmental Siting Scale Models for Technologies

ENVIRONMENTAL OBJECTIVES DEVELOPMENT

MULTIMEDIA ENVIRONMENTAL GOALS (MEGs) PROVIDE ASSESSMENT ALTERNATIVES

- MINIMUM ACUTE TOXICITY EFFLUENT (MATE)
- EXISTING AMBIENT STANDARDS (ES)
- ESTIMATED PERMISSIBLE CONCENTRATIONS (EPC)
- NATURAL BACKGROUND/ELIMINATION OF DISCHARGE (NB)
- BEST TECHNOLOGY (BT)

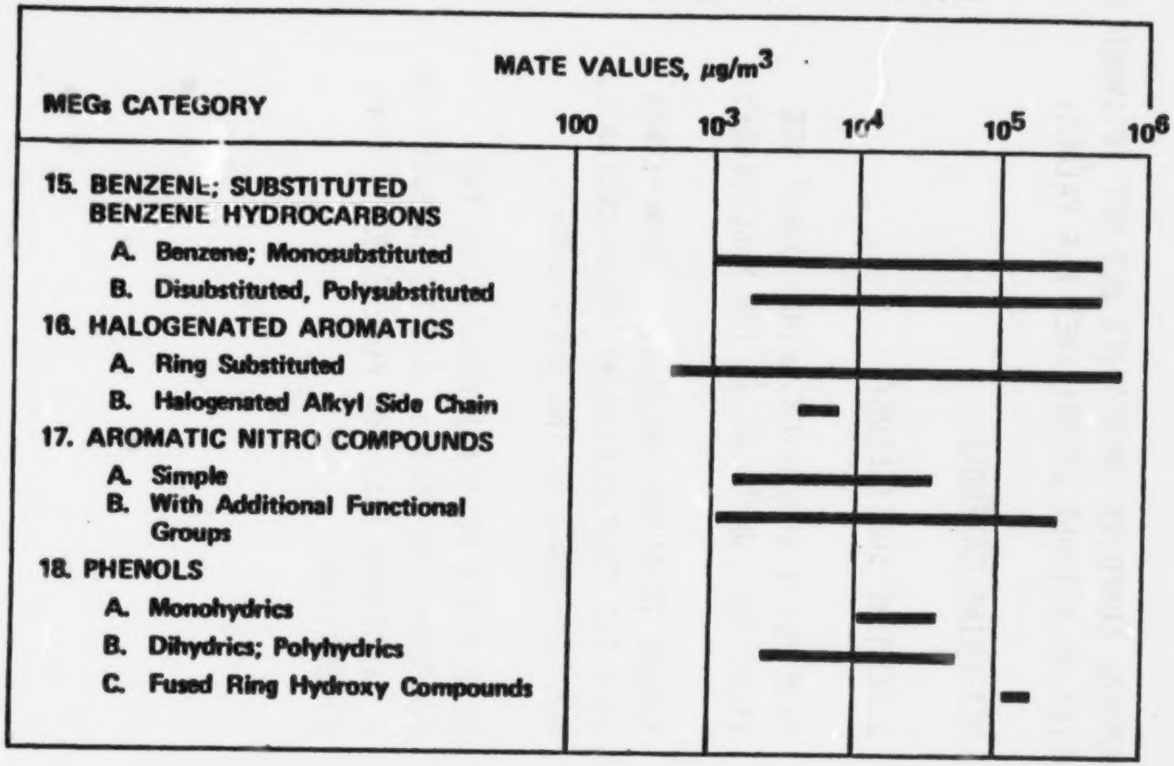
ENVIRONMENTAL OBJECTIVES DEVELOPMENT


MULTIMEDIA ENVIRONMENTAL GOALS (MEGs)
CHEMICAL POLLUTANTS
COMPLEX-EFFLUENT BIOLOGICAL RESPONSE LEVELS
(BIOASSAY CRITERIA)
PHYSICAL FACTORS
(HEAT; NOISE; MICRO-ORGANISMS; RADIONUCLIDES; NONIONIZING RADIATION; WATER- OR LAND-RELATED PHYSICAL FACTORS)
BASED ON AMBIENT FACTORS*
BASED ON TECHNOLOGY*

MOST ACTIVE AREAS ARE SHADED.

*INCLUDES EXISTING STANDARDS

EXAMPLE: SUMMARY OF AIR-HEALTH MATE VALUES



APPLICATION OF MEG'S CATEGORIES:

FOR CHEMICAL COMPOUND IDENTIFIED BUT NOT INCLUDED IN MEG'S LIST OR WITHOUT ESTABLISHED MEG VALUES:

1. DETERMINE CATEGORY.
2. DETERMINE SUBCATEGORY.
3. FROM MEG'S SUMMARIES, FIND LOWEST MEG VALUE FOR COMPOUNDS IN THE SUBCATEGORY.
4. ASSUME THAT MEG VALUE WILL BE NO LOWER THAN THE MOST STRINGENT VALUE INDICATED FOR COMPOUNDS IN THE SUBCATEGORY.
5. SEND RTI A POSTCARD CONCERNING THE COMPOUNDS SO THAT IT MAY BE INCLUDED IN A CANDIDATE LIST FOR FUTURE MEG'S CONSIDERATION.

EXAMPLE OF NUMBERING SYSTEM FOR ORGANIC COMPOUNDS

CATEGORY 18 – – – – – – PHENOLS

18A – – – – – – – MONOHYDRICS

18A020	PHENOL
18A040	CRESOLS
18A060	2-METHOXYPHENOL
18A080	ETHYLPHENOLS
18A100	PHENYLPHENOLS
18A120	2,2'-DIHYDROXYDIPHENYL
18A140	XYLENOLS

MULTIMEDIA ENVIRONMENTAL GOALS

- VOLUMES 1 & 2 AVAILABLE NOVEMBER 1977 (EPA-600/7-77-136A, B)
  - INITIAL METHODOLOGY ESTABLISHED
  - MASTER LIST OF 650 POLLUTANTS PRESENTED
  - 216 CHEMICALS ADDRESSED

- VOLUMES 1A, 3, 4 TO BE AVAILABLE EARLY 1979
  - MINOR REVISIONS IN METHODOLOGY INTRODUCED
  - MEGs POLLUTANT IDENTIFICATION NUMBERS ASSIGNED
  - > 500 ORGANIC COMPOUNDS ADDRESSED

- EXPANDED INORGANICS MEGs AVAILABLE IN 1979
  - COMPUTER-GENERATED

CONTROL TECHNOLOGY
ASSESSMENT

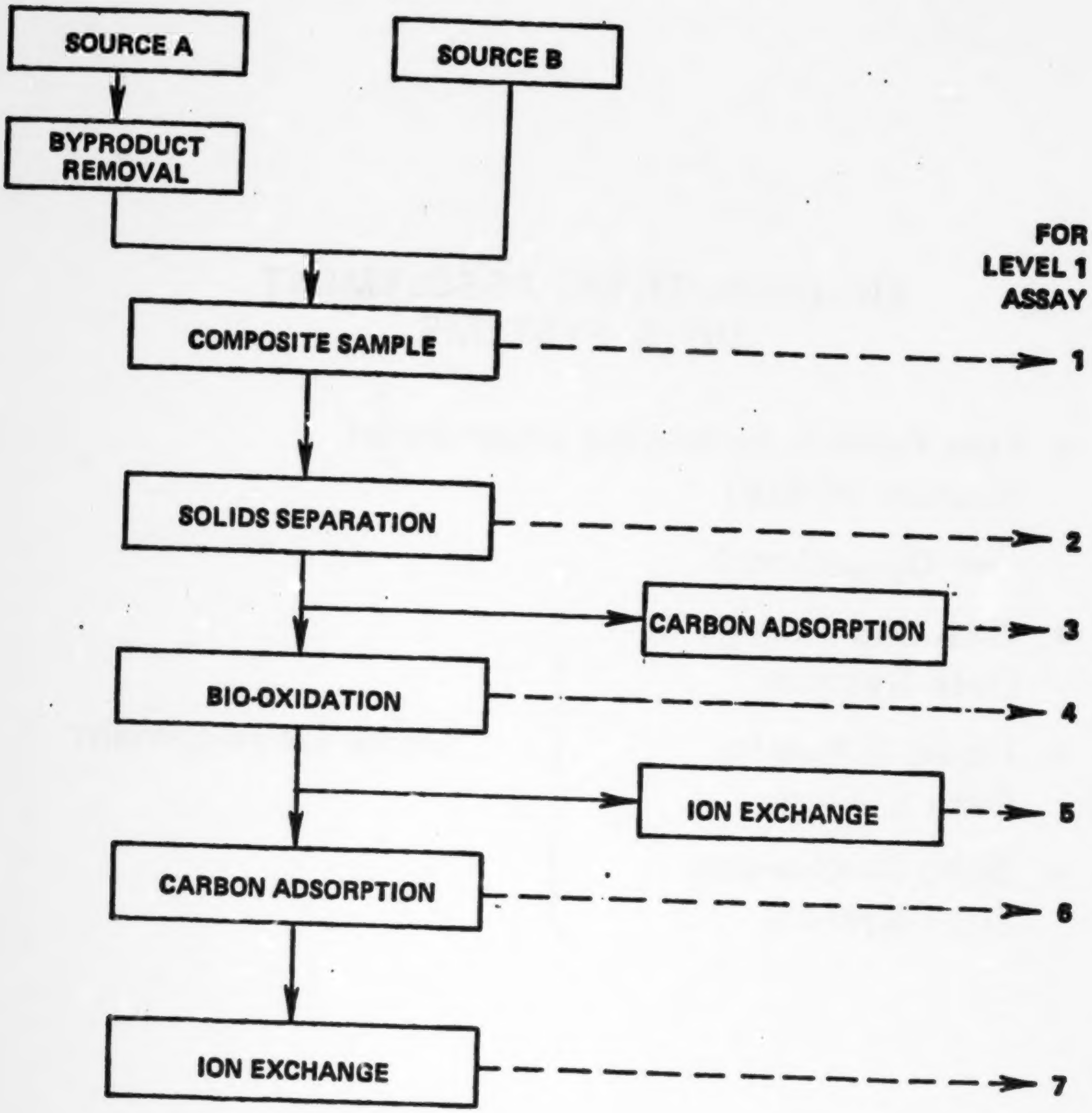
- GAS TREATMENT
- LIQUIDS TREATMENT
- SOLIDS TREATMENT
- FINAL DISPOSAL
- PROCESS MODIFICATION
- COMBUSTION MODIFICATIONS
- FUEL CLEANING
- FUGITIVE EMISSIONS CONTROL
- ACCIDENTAL RELEASE TECHNOLOGY

CONTROL TECHNOLOGY ASSESSMENT

- CONTROL ASSAY DEVELOPMENT
    - FOR USE WITH LEVEL 1
    - PROCEDURES FOR WATER EFFLUENTS ARE DEFINED AND WILL REQUIRE FURTHER DEVELOPMENT AND EVALUATION THROUGH APPLICATION
    - CONCEPT FOR GASEOUS EMISSIONS DEFINED
    - NO WORK YET ON SOLID WASTE/LAND DISPOSAL ASPECTS

- MULTIMEDIA ENVIRONMENTAL CONTROL ENGINEERING HANDBOOK
    - FIRST DRAFT BEING REVIEWED INCLUDES EXTENSIVE ORGANIZED CONTROL DEVICE LISTINGS
    - INITIALLY WILL CONTAIN ONLY ABOUT 100 SPECIFIC DEVICE DATA SHEETS

CONTROL ASSAY DEVELOPMENT TEST SEQUENCE FOR WASTEWATER

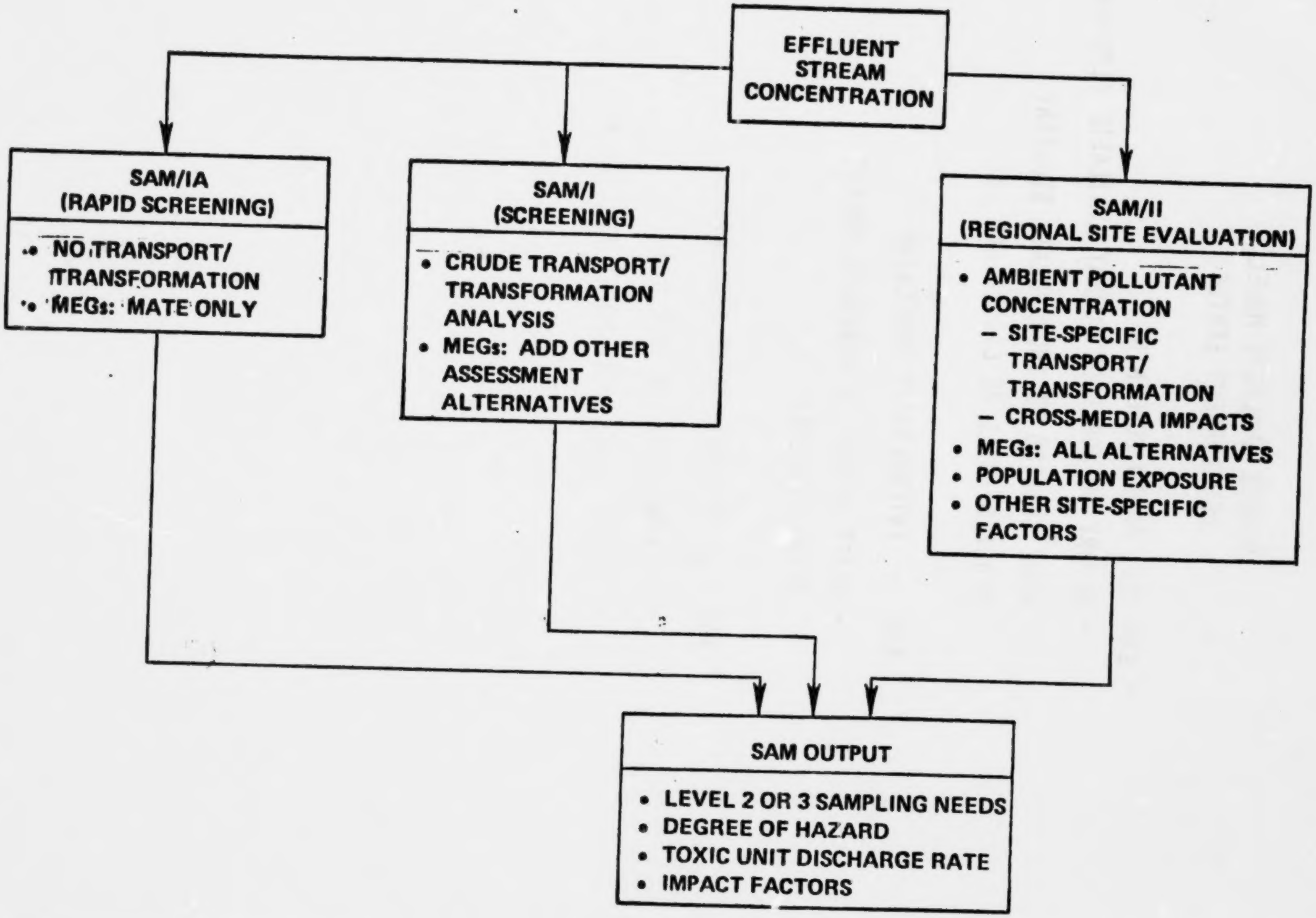


ENVIRONMENTAL ASSESSMENT DATA SYSTEMS

- Fine Particle Emissions Information System (FPEIS)
    - — Operational
- Gaseous Emissions Data System
- Liquid Effluents Data System
- Solid Discharges Data System

Under Development

SCOPE OF SOURCE ANALYSIS MODELS



EFFLUENT STREAM CONCENTRATION

SAM/IA (RAPID SCREENING)

- NO TRANSPORT/ TRANSFORMATION
- MEGs: MATE ONLY

SAM/I (SCREENING)

- CRUDE TRANSPORT/ TRANSFORMATION ANALYSIS
- MEGs: ADD OTHER ASSESSMENT ALTERNATIVES

SAM/II (REGIONAL SITE EVALUATION)

- AMBIENT POLLUTANT CONCENTRATION
  - SITE-SPECIFIC TRANSPORT/ TRANSFORMATION
  - CROSS-MEDIA IMPACTS
- MEGs: ALL ALTERNATIVES
- POPULATION EXPOSURE
- OTHER SITE-SPECIFIC FACTORS

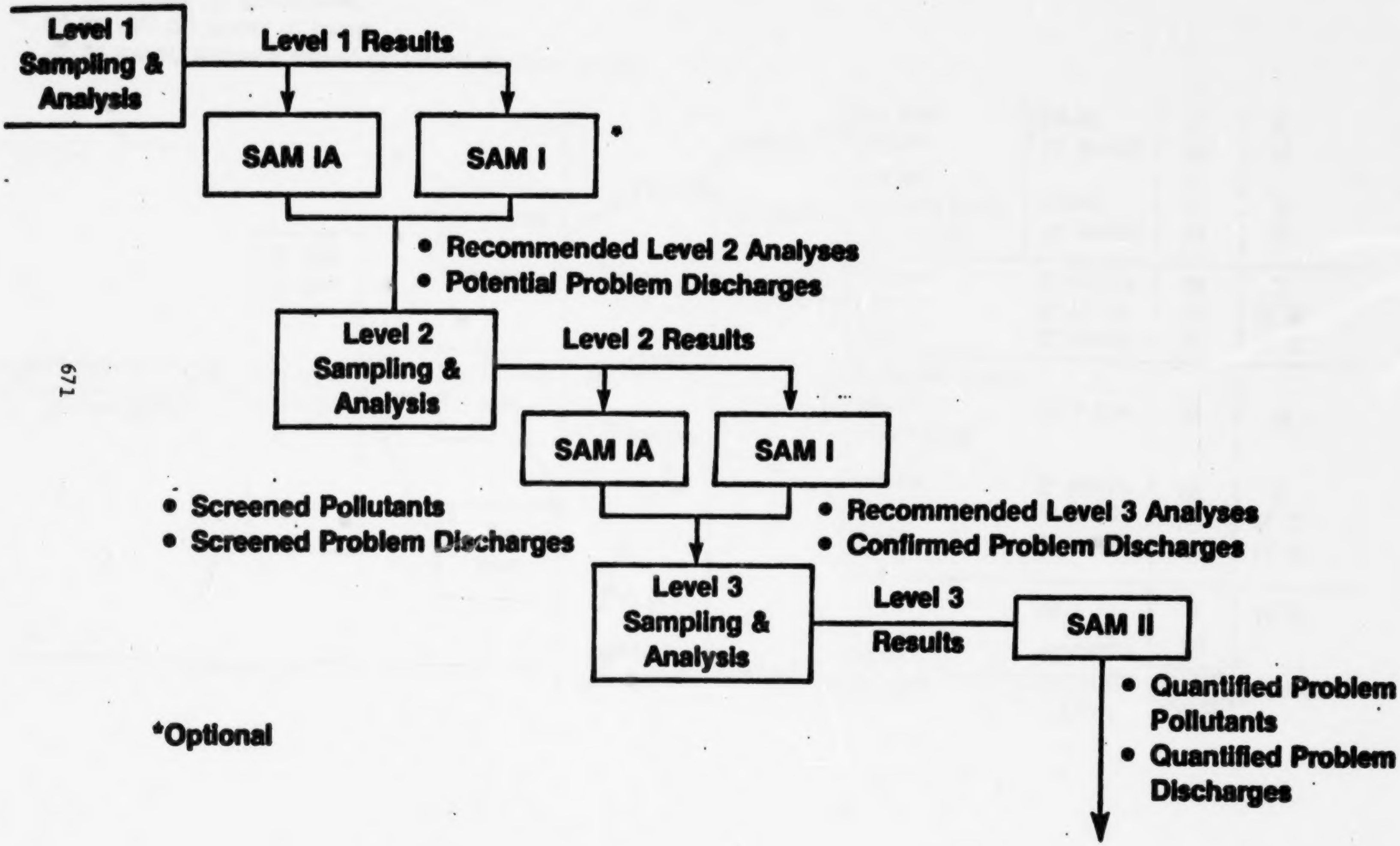
SAM OUTPUT

- LEVEL 2 OR 3 SAMPLING NEEDS
- DEGREE OF HAZARD
- TOXIC UNIT DISCHARGE RATE
- IMPACT FACTORS

SOURCE ANALYSIS MODEL
DEVELOPMENT STATUS

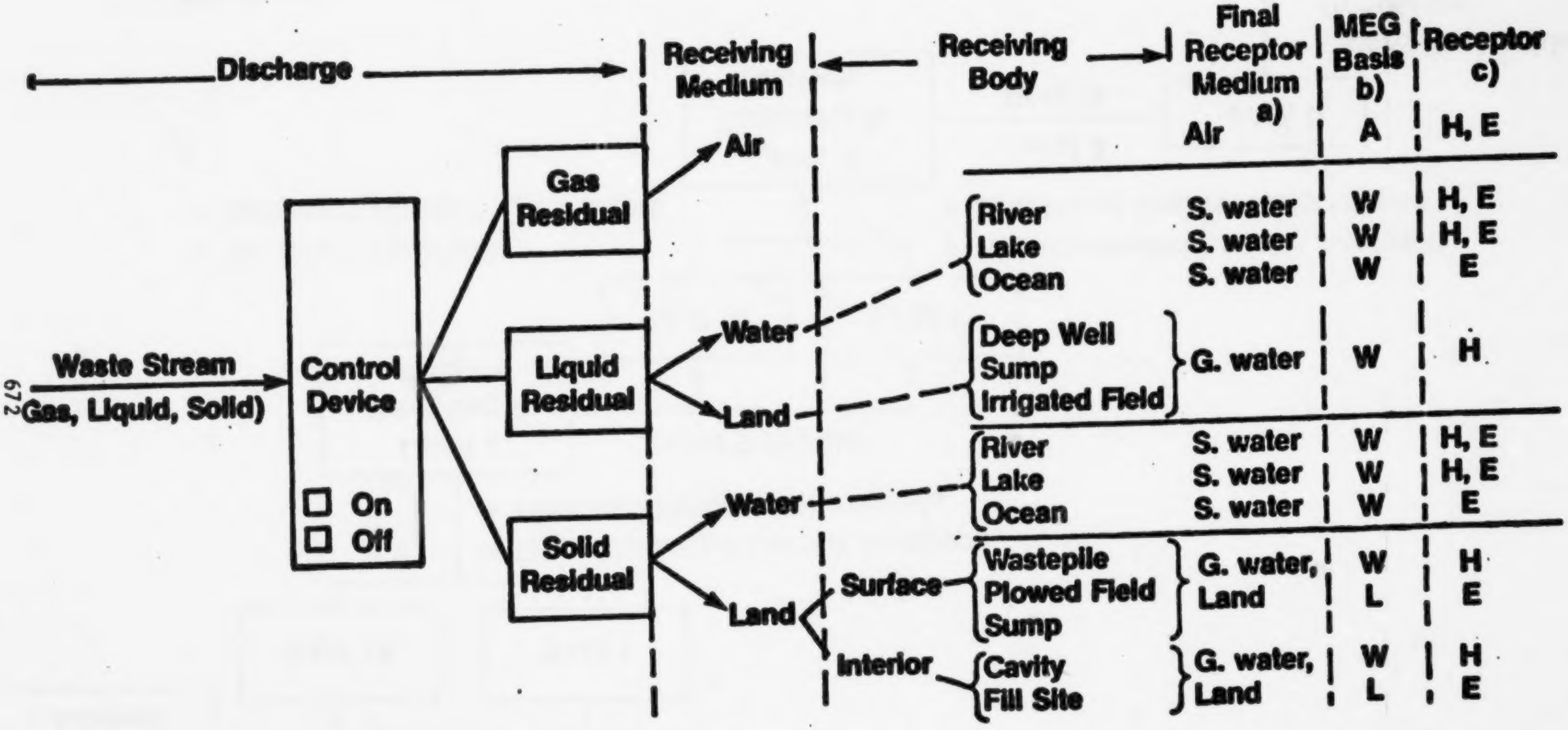
- SAM IA: RAPID SCREENING
  - REPORT IN WORKBOOK FORMAT AVAILABLE (EPA-600/7-78-015)
  - WORK STARTED TO INCORPORATE BIOASSAY RESULTS (WILL BE CALLED SAM IB)
- SAM I: INTERMEDIATE SCREENING
  - DRAFT REPORT IN WORKBOOK FORMAT BEING REVIEWED
- SAM II: REGIONAL SITE EVALUATION
  - NO WORK DONE ON THIS YET
  - SOURCE ASSESSMENT MODEL AVAILABLE

APPROACH FOR APPLICATION OF SAM'S TO PHASED CHEMICAL ANALYSIS


Level 1 Sampling & Analysis
Level 1 Results
SAM IA
SAM I *
• Recommended Level 2 Analyses
• Potential Problem Discharges
Level 2 Sampling & Analysis
Level 2 Results
SAM IA
SAM I
• Screened Pollutants
• Screened Problem Discharges
• Recommended Level 3 Analyses
• Confirmed Problem Discharges
Level 3 Sampling & Analysis
Level 3 Results
SAM II
• Quantified Problem Pollutants
• Quantified Problem Discharges

*Optional

SAM I POLLUTANT DISCHARGE OVERVIEW



a) S. water: Surface water, G. water: Ground water
b) A: Air, W: Water, L: Land
c) H: Health, E: Ecological

OUTPUT OBJECTIVES FOR ENVIRONMENTAL ASSESSMENT

- DEFINED RESEARCH DATA BASE FOR STANDARDS
- QUANTIFIED CONTROL R&D NEEDS
- QUANTIFIED CONTROL ALTERNATIVES
- QUANTIFIED MEDIA DEGRADATION ALTERNATIVES
- QUANTIFIED NONPOLLUTANT EFFECTS AND SITING CRITERIA ALTERNATIVES

KEY E.A.-RELATED REPORTS

- STANDARDS SUPPORT PLAN
- POLLUTION CONTROL GUIDANCE DOCUMENT
- SOURCE TEST AND EVALUATION REPORT
- ENVIRONMENTAL ASSESSMENT REPORT

STANDARDS SUPPORT PLAN (SSP)

- INTRODUCTION
- DEFINITION OF TECHNOLOGIES
- THE STANDARDS SUPPORT SCHEDULE
- DISCUSSION OF THE STANDARDS SUPPORT SCHEDULE
  - PROJECTED DEVELOPMENT OF TECHNOLOGIES
  - REQUIREMENTS OF THE EPA ACTS
  - EPA PLANS FOR REGULATORY ACTIVITIES
  - EPA RESEARCH AND DEVELOPMENT ACTIVITIES
  - PROGRAM OFFICE VIEWS OF R&D DATA NEEDS

POLLUTION CONTROL GUIDANCE DOCUMENT (CGD)

- POLLUTANTS AND PROCESS SOURCES
- ENVIRONMENTAL EFFECTS OF KNOWN POLLUTANTS
- POLLUTION CONTROL TECHNOLOGY
- POLLUTANT DISCHARGE LIMITS
- FUTURE DEVELOPMENT OF EFFLUENT AND EMISSION STANDARDS
- EFFLUENT AND EMISSION MONITORING

ENVIRONMENTAL ASSESSMENT

SOURCE TEST AND EVALUATION REPORT (LEVEL 1)

PRESSURIZED FBC MINIPLANT (EXAMPLE)

- SUMMARY
- PLANT DESCRIPTION
- SAMPLING METHODOLOGY
- ANALYTICAL PROCEDURES
- TEST RESULTS
- CONCLUSIONS AND RECOMMENDATIONS

ENVIRONMENTAL ASSESSMENT REPORT (EAR)

- PROCESS DESCRIPTION OF THE SYSTEMS MAKING UP THE TECHNOLOGY
- CHARACTERIZATION OF INPUT MATERIALS, PRODUCTS, AND WASTE STREAMS
- PERFORMANCE AND COST OF CONTROL ALTERNATIVES
- ANALYSIS OF REGULATORY REQUIREMENTS AND ENVIRONMENTAL IMPACTS BY MEDIA WITH REGIONAL CONSIDERATIONS
- SUMMARY OF THE NEEDS FOR ADDITIONAL DATA TO SUPPORT STANDARDS DEVELOPMENT, ENFORCEMENT, HEALTH AND ECOLOGICAL EFFECTS RESEARCH, AND CONTROL TECHNOLOGY R&D

BARRIERS TO
EA METHODOLOGY IMPLEMENTATION

- COMPLEXITY OF POTENTIAL PROBLEMS
- DIFFICULTIES IN CROSSING DISCIPLINARY AND ORGANIZATION LINES
- BRIDGING THE GAP BETWEEN THE SCIENCES AND ENGINEERING
- DIFFICULTIES IN CHANGING FROM SET PATTERNS AND TRADITIONAL APPROACHES
- RELUCTANCE TO USE AVAILABLE EFFECTS DATA
- LACK OF REALIZATION OF THE IMPORTANCE OF COMMON BASES TO PROMOTE COMMUNICATION AND EVOLUTIONARY IMPROVEMENT OF METHODOLOGIES
- AREAS NEEDING FURTHER RESEARCH

EMPHASIS ON PRACTICAL GOALS

- ENVIRONMENTAL ASSESSMENT (EA) STUDIES NEED TO DO SOMETHING MORE THAN EMPHASIZE TRADITIONAL PROBLEMS THAT HAVE BEEN THE SUBJECT OF YEARS OF INVESTIGATION.

- APPROACH MUST BE DESIGNED TO UTILIZE AVAILABLE OR READILY OBTAINABLE INFORMATION; I.E., APPROACHES MUST BE PRACTICAL.

- ABSOLUTE ANSWERS NOT POSSIBLE; THEREFORE, RELATIVE OR COMPARATIVE ANSWERS DEFINING THE RELATIVE BEST WAYS OF CONTROLLING OR RELATIVE COMPARISONS OF WASTE STREAMS AND SOURCES ARE NECESSARY.

STATE OF KNOWLEDGE/GAPS

- AN EA METHODOLOGY IS EVOLVING OUT OF NECESSITY.

- NEED TO EMPLOY COST-EFFECTIVE APPROACHES TO EFFECT BROAD-COVERAGE SCREENING INITIALLY AND DETAILED SCREENING SUBSEQUENTLY TO FOCUS ON AREAS OF CONCERN.

- APPROACHES MUST BE SUBJECT TO CONTINUED REFINEMENT AND IMPROVEMENT BASED ON EXPERIENCE IN PERFORMING EA STUDIES.

- LONG LEAD TIMES MUST BE DEALT WITH IN DEVELOPING AND IMPLEMENTING METHODOLOGY.

- METHODOLOGY MUST TAKE INTO ACCOUNT PRESENT EA PROGRAM OFFICE AREAS OF CONCERN; E.G., POLLUTANT LISTS, STANDARDS.

ULTIMATE ANSWERS

- ACCEPT THAT THE ONE-POLLUTANT-AT-A-TIME APPROACH TAKES DECADES OF TIME TO BUILD POSSIBLE PROOF OF CHRONIC EFFECTS FOR AN EXTREMELY LIMITED SET OF POLLUTANTS AND THEREFORE HAS SEVERE LIMITATIONS FOR CONTROL DEVELOPMENT GUIDANCE.

- PROVIDE REAL-TIME GUIDANCE AND FILL IN EFFECTS-DATA GAPS FOR CONTROL TECHNOLOGY DEVELOPMENT, EVALUATION, AND DESIGN BY EMPHASIZING USE OF SHORT-TERM EXPOSURE TOXICITY DATA IN EVALUATING EFFLUENTS DIRECTLY.

  POSSIBLE TOXICITY DATA SOURCES ARE:

  - COMPLEX EFFLUENT BIOASSAYS,
  - SIMILAR DATA AVAILABLE IN THE LITERATURE,
  - EXPERIMENTS FOR SPECIFIC CHEMICAL SUBSTANCES OR CLASSES OF SUBSTANCES.

- TAKE BEST ADVANTAGE OF EXISTING EA METHODOLOGY BY MAXIMIZING COMMUNICATION OF PROCEDURES, REFINEMENT IN PROCEDURES, AND RESULTS OF INDIVIDUAL STUDIES.

- MAXIMIZE SUPPORT FROM THE ENVIRONMENTAL SCIENCES LABS IN DEVELOPING EA METHODOLOGY.

- INTEGRATE KEY EPA PROGRAM OFFICE ASPECTS AND METHODOLOGIES.

- DEVOTE RESOURCES TO DEVELOPMENT, STANDARDIZATION, AND COORDINATION OF EA METHODOLOGY.

REVIEW OF REGULATIONS AND STANDARDS INFLUENCING COAL CLEANING

P. Van Voris[1], R. A. Ewing[1], and J. W. Harrison[2]

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ABSTRACT

With the growing public concern over health and ecological effects of man-generated wastes has come increased legislation which places strict regulations and standards for the release of potentially hazardous materials. Although some of this environmental legislation may not be directed specifically toward the coal cleaning industry itself, the Federal acts nevertheless encompass and embrace the industry completely. Thus, these regulations and standards that have been adopted by the United States, as well as Canada, France, Norway, and Sweden, have required the industry to invest a great deal of time and money in the development and installation of pollution control devices or technologies for the proper disposal of wastes.

In this review the following Federal acts, which constitute the primary regulatory authority governing pollution from activities associated with coal cleaning processes, are examined.

Air Pollution	
Clean Air Act of 1970	(P.L. 91-604)
Energy Supply and Environmental Coordination Act of 1974	(P.L. 93-319)
Clean Air Act Amendments of 1977	(P.L. 95-95)
Water Pollution	
Federal Water Pollution Control Act Amendments of 1972	(P.L. 92-500)
Clean Water Act of 1977	(P.L. 95-217)
Solid Waste	
Solid Waste Disposal Act of 1965	(P.L. 89-272)
Resource Recovery Act of 1970	(P.L. 91-512)
Resource Conservation and Recovery Act of 1976	(P.L. 94-580)

All of the above acts are administered and enforced by the U.S. Environmental Protection Agency and are embodied in Title 40 of the Code of Federal Regulations.

The applicability of the provisions of these acts to the coal cleaning industry, as well as some specific state regulations, are examined. This, along with a critique of Federal acts which at this time only have potential applicability, constitute the body of this report.

INTRODUCTION

During the past half century, increased industrialization, product demand, additional leisure time, and population growth have given rise to an increased use of energy. Both the U.S. Environmental Protection Agency and the Department of Energy have developed a series of energy scenarios showing that energy needs may grow from our current annual consumption of approximately 75 Quads (1 Quad = 1 x 10^{15} Btu) of energy to a conservative estimate of nearly 110 Quads by the year 2000. Coal is currently supplying 24 percent of the total Quads and is predicted to supply 33 percent by the turn of the century. The overall projected increase in United States energy usage is approximately 46 percent, in relation to only a 21 percent expected increase in the U.S. population size (U.S. Department of Commerce, 1977). Other, more pessimistic projections (Ehrlich et al., 1973; Hardin, 1973; and Garvey, 1972) have painted even more startling scenarios showing energy consumption doubling in the next quarter century.

With this increased demand for energy came man's understanding that the earth is a finite structure that must support a broad diversity of life for an infinite amount of time. This realization, along with the recognition of the environmental blight that man had previously caused, gave birth to environemtnal concerns which, in turn, spawned governmental regulations and their subsequent promulgation designed to help ensure the preservation of the ecosystems and their inhabitants.

Because of the projected increase in our reliance on coal as one of the primary energy sources for our country, as well as the potential role of coal cleaning in reducing environmental risks associated with coal, it was felt that a review of the major federal regulations affecting the coal preparation industry was necessary. This review is divided into the key areas of regulatory control— air, water and solids— and each is examined both at the federal and state levels.

REGULATIONS AFFECTING COAL CLEANING

In order to evaluate the existing and pending environmental regulations that will affect coal cleaning, several reviews of Federal and State regulations governing pollution resulting from activities associated with coal cleaning, transportation, storage, and handling have been prepared (Ewing et al., 1977; Cleland and Kingsbury, 1977; Energy and Environmental Analysis, Inc., 1976; Harrison, 1978; and Ewing et al., 1978). The scope of these reviews included the regulations influencing the combustion of coal as a fuel but excluded those for the conversion of coal to coke or to liquid or gaseous fuels. The results of the most recent review (Ewing et al., 1978) are the basis for this paper and, unfortunately, will be outdated by the time this has been published. Therefore, repeated updates of this report are planned as a portion of the U.S. EPA Technological and Environmental Assessment of Coal Cleaning Processes program.

The following Federal acts constitute the primary regulatory authority governing pollution resulting from activities associated with coal cleaning processes.

Primary Regulatory Authority
Governing Pollution Resulting
From Coal Cleaning Processes

Air Pollution	
Clean Air Act of 1970	(P.L. 91-604)
Energy Supply and Environmental Coordination Act of 1974	(P.L. 93-319)
Clean Air Act Amendments of 1977	(P.L. 95-95)
Water Pollution	
Federal Water Pollution Control Act Amendments of 1972	(P.L. 92-500)
Clean Water Act of 1977	(P.L. 95-217)
Solid Waste	
Solid Waste Disposal Act of 1965	(P.L. 89-272)
Resource Recovery Act of 1970	(P.L. 91-512)
Resource Conservation and Recovery Act of 1976	(P.L. 94-580)
U.S. Geological Survey - Department of Interior	Title 30 CFR, Part 211

Potentially applicable for Chemical Coal Cleaning - Toxic Substances Control Act of 1976 (P.L. 94-469).

These acts are embodied in Title 40 of the Code of Federal Regulations and their applicability to coal cleaning is discussed in the following sections.

State regulations are generally written or amended to incorporate, as a minimum, the provisions of the Federal laws. In some instances, state regulations are more stringent than Federal regulations. The states are usually required to submit implementation plans for U.S. EPA approval outlining how Federal standards will be met and specifying a reasonable time frame for implementing those standards. This state certification procedure is essentially complete for air pollution, well underway for water pollution, and just beginning for solid wastes.

Air Pollution Regulations

Federal

The development and implementation of air pollution controls have been approached in two different ways by the U.S. Environmental Protection Agency in accordance with the provisions of the Clean Air Act of 1970. Source emission standards are designed to regulate the quantities of pollutants emitted from point sources, whereas ambient air quality standards are designed to regulate the concentrations of pollutants in the atmosphere.

Ambient Air Quality Standards. The U.S. EPA, under Section 109 of the Clean Air Act of 1970, has established national primary and secondary ambient air quality standards (NAAQS) that regulate pollutant levels in order to protect, respectively, human health and public welfare (property and plant and animal life) (U.S. Environmental Protection Agency, 1977a).

Implementation is the responsibility of the individual states, under a State Implementation Plan (SIP), which must be approved by the U.S. EPA. Also, the permissible levels for certain named pollutants (criteria pollutants), which the SIP must provide will not be exceeded, are established by the U.S. EPA. Some of these "criteria pollutants" arise mainly from motor vehicles; however, pollutants such as total suspended particulates, sulfur oxides, and nitrogen oxides, arise from stationary sources and are released mainly through coal combustion. Current national ambient air quality standards for the criteria pollutants are summarized in Table 1 (U.S. Environmental Protection Agency, 1977a).

Table 1. National ambient air quality standards

	Averaging Period	Primary	Secondary
Particulates	Annual geometric mean	75 $\mu g/m^3$	60 $\mu g/m^3$
	Max. 24-hr concentration, not to be exceeded more than once per year	260 $\mu g/m^3$	150 $\mu g/m^3$
Sulfur dioxide	Annual arithmetic mean	80 $\mu g/m^3$ (0.03 ppm)	60 $\mu g/m^3$ (0.02 ppm)
	Max. 24-hr concentration, not to be exceeded more than once per year	365 $\mu g/m^3$ (0.14 ppm)	260 $\mu g/m^3$ (0.1 ppm)
	Max. 3-hr concentration, not to be exceeded more than once per year	--	1300 $\mu g/m^3$ (0.5 ppm)

Table 1. (Continued)

	Averaging Period	Primary	Secondary
Carbon monoxide	Max. 8-hr concentration, not to be exceeded more than once per year	10 mg/m^3 (9 ppm)	10 mg/m^3 (9 ppm)
	Max. 1-hr. concentration, not to be exceeded more than once per year	40 mg/^{3} (35 ppm)	40 mg/m^3 (35 ppm)
Hydrocarbons	Max. 3-hr (6-9 A.M.) concentration, not to be exceeded more than once a year	160 μg/m^3 (0.24 ppm)	160 μg/m^3 (0.24 ppm)
Photochemical oxidants	Annual arithmetic mean	--	--
	Max. 4-hr concentration	--	--
	Max. 1-hr concentration, not to be exceeded more than once per year	160 μg/m3 (0.08 ppm)	160 μg/m3 (0.08 ppm)
Nitrogen dioxide	Annual arithmetic means	100 μg/m3 (0.05 ppm)	100 μg/m3 (0.05 ppm)

New Source Performance Standards. In accordance with Section 111 of the 1970 Clean Air Act, the U.S. EPA is required (1) to compile a list of categories of emission sources that may contribute significantly to air pollution and (2) to establish Federal standards of performance for new and modified stationary sources in such categories. Unlike the ambient air quality standards, these standards of performance are not based on the effects of pollutants on public health and welfare but on "the degree of emission limitation achievable through the application of the best system of emission reduction which (taking into account the cost of achieving such reduction) the Administrator determines has been adequately demonstrated".* Agency terminology for this is BACT (Best Available Control Technology).

Standards have now been promulgated for over 25 types of sources. The foremost category on the list is fossil-fuel-fired stationary sources; many provision of the Clean Air Act Amendments of 1977 are aimed specifically at such sources, and the restrictions applied are much more rigorous than in the past. Where the original New Source Performance Standard (NSPS) for large [>250 million Btu/hr (73 MW)] coal-fired boilers permitted the emission of 1.2 lb SO_2/million Btu, the amended Act specifies, in addition, that the revised NSPS "...shall reflect the degree of emission limitation and the percentage reduction achievable through application of the best technological system of continuous emission reduction ...", i.e., a percentage reduction will be required rather than maintenance of emissions below an upper limit. A comparison of the newly-released revised NSPS and existing NSPS is presented in Table 2. The criteria are tempered by the usual energy, cost, and environematnal impact considerations. Also, credit may be taken for any cleaning of the fuel or reduction in the pollution characteristics of the fuel after extraction (i.e., mining) and before combustion.

Since NSPS's for fossil-fuel-fired boilers apply only to units above 250 million Btu/hr (73 MW), very few boilers employed

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*However, it should be noted that the setting of NAAQS provides the justification for setting emissions standards for these pollutants.

Table 2. Comparisons of existing NSPS and revised NSPS

	Existing NSPS	Revised NSPS*
SO_2	1.2 lb/million Btu	0.2 lb/million Btu** 85% reduction
Particulates	0.1 lb/million Btu	0.03 lb/million Btu 99% reduction from uncontrolled sources
NO_x	0.7 lb/million Btu	0.6 lb/million Btu 65% reduction from uncontrolled sources

Currently no NSPS for Industrial Boilers

*U.S. Environmental Protection Agency, 1978a.

**Limits for no more than 1.2 lb/10^6 Btu with 0.2 lb/10^6 as the floor.

in coal cleaning activities (thermal dryers) will be affected by these new standards. On the other hand, many, if not most, of the potential utility users of coal employ boilers of this size or larger. Thus, depending somewhat on the SO_2 regulations finally promulgated, the revisions to the NSPS for fossil-fuel-fired boilers will have a significant, but direct, impact upon coal cleaning. The role of coal cleaning in the utilization of coal undoubtedly will be influenced materially, although the way in which this will be manifested is as yet unclear. The percentage reductions required are unlikely to be achieved by coal cleaning alone, so some supplemental form of SO_2 removal will probably be required. On the other hand, the converse may also be true, especially on high sulfur coal, so coal cleaning may be technically desirable (and probably also economically and environmentally advantageous) to supplement flue gas desulfurization.

New source performance standards that are directly applicable to coal cleaning processes are those for new and modified coal preparation plants and handling facilities which include: thermal dryers, pneumatic coal cleaning equipment (air tables), coal processing and conveying equipment (including breakers and crushers), coal storage systems (except for open coal storage piles), and coal transfer and loading systems (including barge loading facilities). Although the regulations in 40 CFR Part 60 (U.S. Environmental Protection Agency, 1977b) do not specify their application elsewhere, the explanatory discussion in the promulgation announcement (41 FR 2232, January 15, 1976) also included other sources that handle large amounts of coal, such as power plants, coke ovens, etc.

These NSPS, which are applicable to all coal preparation or handling facilities processing more than 200 tons/day, include (U.S. Environmental Protection Agency, 1977b):

- emissions from thermal dryers—may not exceed 0.070 gr/dscm (0.031 gr/dscf) and 20 percent opacity
- emissions from pneumatic coal cleaning equipment—may not exceed 0.040 gr/dscm (0.018 gr/dscf) and 10 percent opacity
- emissions from any coal processing and conveying equipment, coal storage system, or coal transfer

and loading system processing coal (nonbituminous as well as bituminous)—may not exceed 20 percent opacity.

Hazardous Pollutant Emission Standards. The atmospheric emission of several hazardous pollutants is already regulated under Section 112 of the Clean Air Act of 1970. Two of these (beryllium and mercury) are found in coal but not at levels such that their emission is expected to violate standards. The establishment of regulations governing arsenic, polycyclic organic matter (POM), and cadmium emissions is now under consideration. A national ambient air quality standard for lead has just been proposed (U.S. Environmental Protection Agency, 1977c). Except for POM's, emissions of the other hazardous pollutants mentioned above (in concentrations likely to be governed by the standards) are expected to be emitted only from sources such as those found in the nonferrous metal industry or from the combustion of leaded gasoline and the standards should have little effect upon coal cleaning processes.

Prevention of Significant Deterioration of Air Quality. A new Part C (Sections 160-169) was incorporated into the Clean Air Act Amendments of 1977 for the prevention of significant deteriorations (PSD) of the present ambient air quality. Three land-use classes are established which are interpreted by the U.S. EPA to have the following types of development:

- Class I - little or no development
- Class II - scattered development
- Class III - concentrated or large-scale development.

Classification in Class I is mandatory for national parks exceeding 6,000 acres in size and wilderness areas. The verbiage is complex and involved, but the significant fact, with respect to coal cleaning processes, is that any new source in an area subject to the provisions of this section is to employ the Best Available Control Technology for each pollutant subject to regulation. Cost considerations for achieving such emission reduction is not invoked as a factor. Thus, the best available control technology required for PSD must be better than those of the NSPS. It is obvious that these are site-specific problems and that a uniform national standard will not be utilized. Each proposed new source will be considered by the affected state on a case-by-case basis under the state implementation plan. The Act provides for maximum allowable increases in SO_2 and particulates for each land-use class, with the provision that the NAAQS will not be exceeded. Allowable pollutant increases are shown for all three land-use classes in Table 3, along with national primary and secondary ambient air quality standards.

Table 3. Allowable pollutant increases above baseline concentrations

	Concentration, μg/m^3				
	Land Class Area			NAAQS	
	I	II	III	Primary	Secondary
Particulate Matter					
Annual geometric mean	5	19	37	75	60
24-hr maximum	10	37	75	260	150

Table 3. (Continued)

	Concentration, µg/m³				
	Land Class Area			NAAQS	
	I	II	III	Primary	Secondary
Sulfur Dioxide					
Annual arithmetic mean	2	20	40	80	60
24-hr maximum	5	91	182	365	260
3-hr maximum	25	512	700	--	1300

Visibility Protection for Federal Class I Areas. Section 169 of Part C specifically addresses the national goal set by the Congress for the prevention of any future (and the remedying of any existing) impairment of visibility in mandatory Federal Class I areas from man-made air pollution. Within 24 months, the Administrator will promulgate regulations to assure reasonable progress toward meeting the national goal. The requirements include existing sources and may require use of the best available retrofit technology.

Nonattainment Areas. A new Part D (Sections 171-178) was also incorporated into the Clean Air Act Amendments of 1977 to address alleviation of air pollution problems in areas where one or more air pollutants exceed any national ambient air standard. Theoretically, no new emission source could be constructed in a nonattainment area. Since this was judged to be an impractical answer, the compromise solution was to require the "lowest achievable emission rate" (LAER). This is an even more restrictive standard than the BACT specified for prevention of significant deterioration and includes either the most stringent emission limitation for such source category in any state implementation plan or the most stringent emission limitation actually achieved in practice, whichever is more stringent, and in no event will it be less restrictive than the NSPS is for that source category. Like the PSD, this is to be implemented by the individual states through the state implementation plans on a case-by-case basis. A key provision is that the states are to continue "reasonable further progress" in order to achieve annual incremental reductions of the applicable air pollutant, including such reduction in emissions from existing sources as may be obtained through the adoption, at a minimum, of "reasonably available control technology" (RACT).

The above is part of the so-called "offset" approach wherein reductions are made in existing emissions to permit addition of a new source, with the additional constraint that an overall decrease should be shown.

In general, designation as a nonattainment area means that an applicable SIP must be revised to provide for the attainment of the NAAQS as expeditiously as possible. The revised SIP must require permits for the construction and operation of major new and modified stationary sources and must prohibit potential new source construction where emissions would contribute to an increase in pollutants for which a NAAQS was already being exceeded.

The U.S. EPA has just published a list of the NAAQS attainment status of all areas within each state (U.S. Environmental Protection Agency, 1978b).

State

Although the U.S. EPA promulgates national ambient air quality standards, states have the privilege of establishing more stringent standards. Thirty-three states and the District of Columbia have ambient air quality standards (AAQS) that are more stringent than those of the Federal Government.

Since the concentrations of nitrogen oxides and other pollutants other than sulfur oxides and particulates, for which there are AAQS, are only marginally related to the quality of coal prepared or burned, emphasis has been placed on the standards for sulfur dioxide and particulate matter (total suspended particulates). Those states with more stringent AAQS are Alaska, Arizona, California, Connecticut, Colorado, Delaware, Florida, Georgia, Hawaii, Indiana, Kentucky, Louisiana, Maine, Maryland, Minnesota, Mississippi, Missouri, Montana, Nevada, New Hampshire, New Mexico, New York, North Carolina, North Dakota, Ohio, Oregon, South Dakota, Tennessee, Vermont, Washington, West Virginia, Wisconsin, and Wyoming (Figure 1).

Water Pollution Regulations

Federal

There are no national ambient water quality regulations analgous to those for air; water pollution is regulated

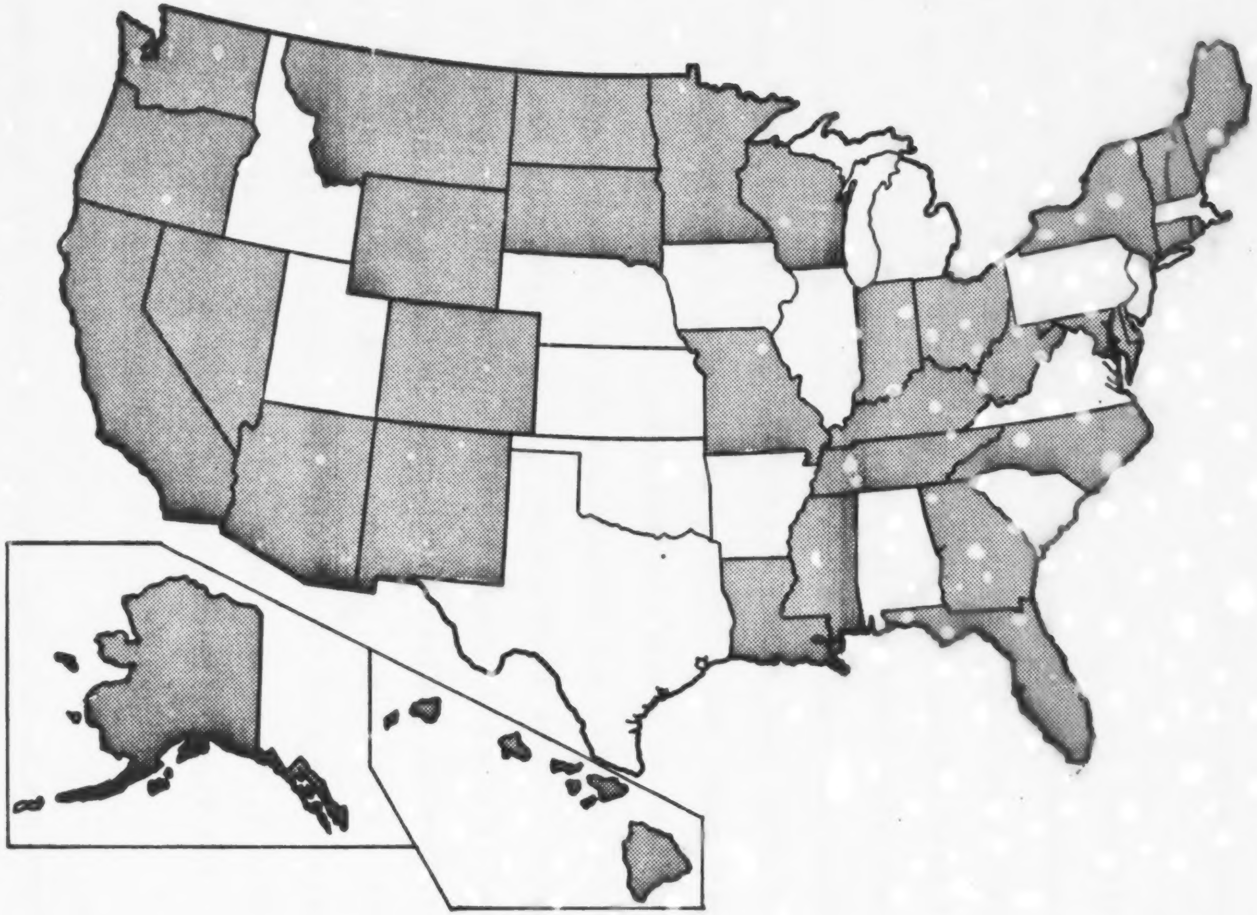

Figure 1. Map showing states with more stringent AAQS than NAAQS.

nationally on the basis of emissions (termed effluents in the case of water).

Effluent Guideline Limitations. The enabling Act providing the authority to establish effluent limitations was the Federal Water Pollution Control Act (FWPCA) amendments of 1972 (P.L. 92-500). Basic effluent limitations have now been promulgated for numerous industries; others have been challenged by the affected industries and are still in abeyance pending further development. The FWPCA was further amended in 1977 (P.L. 95-217). Effluent guidelines are presently based on the best practicable control technology currently available (BPCTCA), which was to have been achieved by July 1, 1977. By July 1, 1983, effluent guideline limitations were to have required the application of the best available technology economically achievable (BATEA). The 1977 amendments have extended this date a year to July 1, 1984.

Effluent guidelines are also being promulgated for new sources. These new source performance standards for wastewater effluents are intended to be the most stringent standards applied.

Federal control of water pollution sources associated with coal preparation and handling is achieved through the issuance to each discharger of NPDES (National Pollutant Discharge Elimination System) permits which contain limits on specific pollutants in the effluents. Effluents from coal cleaning are regulated as a part of the coal mining point source category (40 CFR, Part 434). This category includes "associated areas" such as the plant yards, immediate access roads, slurry ponds, drainage ponds, coal refuse piles, and coal storage piles and facilities. Regulations have been divided into two groups—one for acidic and one for alkaline wastes. Regulations for existing plants (U.S. Environmental Protection Agency, 1977d) and proposed new source performance standards (U.S. Environmental Protection Agency, 1977e) are summarized in Table 4. Final regulations for BATEA effluent limitations have not yet been promulgated.

Table 4. Effluent limitations for coal preparation plants

Effluent Characteristic	Acidic Wastes[a,b]		Alkaline Wastes[a]	
	Daily Maximum	30-Day Average	Daily Maximum	30-Day Average
		Existing Sources		
TSS, mg/1	70.0	35.0	70.0	35.0
Iron, toal, mg/1	7.0	3.5	7.0	3.5
Manganese, total, mg/1	4.0	2.0	--	--
pH	6.0-9.0		6.0-9.0	
		Proposed New Source Performance Standards[c]		
TSS, mg/1	70.0	35.0	70.0	35.0
Iron, total, mg/1	3.5	3.0	3.5	3.0
Manganese, total, mg/1	4.0	2.0	--	--
pH	6.0-9.0		6.0-9.0	

(a) Excess water effluent from a facility designed to contain or treat the volume of water from the 10-year, 24-hour precipitation event is not subject to limitations.

(b) pH may be slightly exceeded to achieve manganese limitation, up to 9.5.

(c) No discharge of pollutants permitted from facilities which do not recycle wastewater for use in processing.

Toxic Pollutants. The Clean Water Act of 1977 introduced a new requirement for the control of toxic pollutants that are required to be limited by the application of the best available technology economically achievable. The initial list of toxic subatances and families of substances contained those identified in the consent decree between the U.S. EPA and the National Resources Defense Council (NRDC). This list, shown in Table 5 (U.S. Environmental Protection Agency, 1978c), comprises principally organic compounds thought to have no connection with coal cleaning. This list has now grown into the current 129 "priority pollutants" of which 24 have been tentatively identified as existing in wastewater from some coal cleaning plants (Randolph, 1978).

However, the listing in Table 5 of a few inorganic compounds (arsenic, beryllium, lead, etc.) would seem, by definition, to place them in the category of pollutants of concern to the coal cleaning industry. No regulations or proposed regulations have yet been published and the potential effects of such limitations of the "priority pollutants" on coal cleaning operations would be speculative at this time.

Water Quality Criteria. While ambient air quality standards are set at the Federal level, water quality standards are primarily a state responsibility. The only existing Federal water quality standards are those for drinking water, applicable to public (community) water supplies. Maximum contaminant levels in public water supplies have been set for contaminants associated

Table 5. Pollutants being considered for effluent limitations

1. Acenaphthene
2. Acrolein
3. Acrylonitrile
4. Aldrin/Dieldrin
5. Antimony and compounds

6. Arsenic and compounds
7. Asbestos
8. Benzene
9. Benzidene
10. Beryllium and compounds

11. Cadmium and compounds
12. Carbon tetrachloride
13. Chlordane
14. Chlorinated benzenes
15. Chlorinated ethanes

16. Chloroalkyl ethers
17. Chlorinated napthalene
18. Chlorinated phenols
19. Chloroform
20. 2-chlorophenol

21. Chromium and compounds
22. Copper and compounds
23. Cyanides
24. DDt and metabolites
25. Dichlorobenzenes

26. Dichlorobenzidine
27. Dichloroethylenes
28. 2,4-dichlorophenol
29. Dichloropropane and dichloropropene
30. 2,4-dimethylphenol

31. Dinitrotoluene
32. Diphenylhydrazine
33. Endosulfan and metabolites
34. Endrin and metabolites
35. Ethylbenzene

36. Fluoranthene
37. Haloethers
38. Halomethanes
39. Heptachlor and metabolites
40. Hexachlorobutadiene

41. Hexachlorocyclohexane
42. Hexachlorocyclopentadiene
43. Isophorone
44. Lead and compounds
45. Mercury and compounds

46. Naphthalene
47. Nickel and compounds
48. Nitrobenzene
49. Nitrophenols
50. Nitrosamines

51. Pentachlorophenol
52. Phenol
53. Phthalate esters
54. Polychlorinated biphenyls (PCB's)
55. Polynuclear aromatic hydrocarbons

56. Selenium and compounds
57. Silver and compounds
58. 2,3,7,8-Tetrachlorodibenzo-p-dioxin
59. Tetrachloroethylene
60. Thallium and compounds

61. Toluene
62. Toxaphene
63. Trichloroethylene
64. Vinyl chloride
65. Zinc and compounds

with coal and coal cleaning activities: arsenic, barium, cadmium, chromium, fluoride, lead, mercury, nitrate, selenium, and silver.

Federal water quality criteria (guidelines) have recently been revised and expanded and published by the U.S. EPA (U.S. Environmental Protection Agency, 1976); while these criteria do not have direct regulatory application, the states are expected to adopt these when implementing state water quality regulations.

Criteria are presented for water quality which will provide for the protection and propagation of fish and other aquatic life and for recreation in and on the water. Criteria are also presented for domestic water supply quality to protect human health.

State

The situation on control of water pollution by the states is analogous to that for air pollution. Emission standards (effluent guidelines) are established on a national level by the U.S. EPA, but their implementation is regarded as a state responsibility. The FWPCA (P.L. 92-500) provides for the reduction of duplicate laws by delegating permit issuance authority to the states. Delegation of authority takes place when a state demonstrates that it has legal capability and resources to operate the program as envisioned by that Federal law. The states of Colorado, Indiana, Kansas, Maryland, Missouri, Montana, North Dakota, Ohio, Virginia, Washington, and Wyoming are delegated NPDES-issuing states. The effluent limitations vary among the delegated and nondelegated states.

Water pollution control enforcement is based on effluent standards rather than stream quality, and plant discharges must be within certain limits prescribed for each industry. The objective of such control systems is to achieve or maintain ambient water quality standards that are primarily a state responsibility. If these are not achieved by compliance with effluent standards, more stringent limits may be applied.

Solid Waste Regulations

Federal

Prior to October 21, 1976, protection of the environment from pollution originating from the land disposal of solid wastes was provided by the Solid Waste Disposal Act of 1965 (P.L. 89-272), as amended by the Resource Recovery Act of 1970 (P.L. 91-512). Federal guidelines for the land disposal of solid wastes are given in Title 40 CFR, Part 241 (U.S. Environmental Protection Agency, 1977f).

Pursuant to Section 211 of the amended Solid Waste Disposal Act, the guidelines are mandatory for Federal agencies and are recommended for state, interstate, regional, and local government agencies for use in their solid waste disposal activities. However, these are only guidelines and do not establish new standards but set forth requirements and recommended procedures to ensure that the design, construction, and operation of the land disposal site is environmentally acceptable. The thrust of Part 241 is directed toward regulation of sanitary and municipal wastes; mining wastes are esentially ignored.

The management of solid and hazardous wastes entered a new era on October 21, 1976, upon passage of the comprehensive Resource Conservation and Recovery Act (RCRA) of 1976 (P.L. 94-580). Although the actual implementation of this Act has not yet occurred, it is already clear that management of such wastes will be revolutionized by the specific regulations currently being drafted by the U.S. EPA.

The introductory section of the Act describes the Federal role as one of providing financial and technical assistance and leadership in the development, demonstration, and application of new and improved methods of waste management. In practice, it appears that guidelines and regulations will be developed by the U.S. EPA for adoption and promulgation by the states, possibly in a fashion similar to the SIP's used for air pollution control. The individual states would enforce their adopted regulations. Some of the general provisions of the Act are:

- The U.S. Environmental Protection Agency is to issue guidelines within 1 year for defining sanitary landfills as the only acceptable land disposal alternative that can be implemented; open dumps are to be prohibited.
- Within 1 year, the U.S. EPA will develop and publish suggested guidelines for solid waste management.
- Within 18 months, the U.S. EPA will promulgate criteria for identifying hazardous waste, standards for generators, transporters, and for treatment, storage, and disposal of hazardous wastes.
- Permit programs are to be managed by the states but under minimum guidelines to be provided by the U.S. EPA.
- Each regulation promulgated will be reviewed and, where necessary, revised not less than every 3 years.

The development of specific solid waste regulations is appreciably behind schedule and discussion of possible requirements for coal cleaning refuse is, accordingly, unavoidably speculative. However, the indications are that coal cleaning refuse may be classified as hazardous waste, a case which would then involve the most restrictive provisions of the Act, including permit application, monitoring, record-keeping, and reporting.

The Geological Survey of the U.S. Department of the Interior has established regulations for the disposal of wastes from coal preparation plants located on land associated with mining (U.S. Department of the Interior, 1977). Preparation is defined as any crushing, sizing, cleaning, drying, mixing, or other processing of coal to prepare it for market. The operator is required to:

> "dispose of all waste resulting from the mining and preparation of coal in a manner designed to minimize, control, or prevent air and water pollution and the hazards of ignition and combustion".

Additionally, more specific requirements are given for waste pile construction, covering and revegetation, and settling ponds.

State

A few states have solid waste disposal regulations directly applicable to coal preparation or consumption. The various states have general regulations covering solid waste management, solid waste disposal, and solid waste disposal areas (landfills, sanitary landfills, etc.). Solid wastes are not to be disposed of in such a manner as to or in those areas where they could endanger human health and plant or animal life or contribute to air pollution. Locations of these disposal areas are also to be such that they pose the least possibility of surface or groundwater contamination. The provisions of the Resource Conservation and Recovery Act of 1976 will allow definitive guidelines to be established by each state for the storage and disposal of solid wastes, including those generated from coal preparation and consumption.

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DEVELOPMENT OF ENVIRONMENTAL ASSESSMENT CRITERIA FOR COAL CLEANING PROCESSES

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ABSTRACT

There are four interrelated activities associated with the environmental impact assessment of coal cleaning facilities. The first step is documentation of chemical characteristics of the waste stream, with the physical transport and distribution characteristics of the pollutants of concern in air, water, and land being the next step. This is then followed by estimations of the biological transport of those pollutants within the ecosystem where the pollutants may reach any number of receptor organisms, including man. The fourth and final activity estimates health and ecological effects relative to the dosages predicted by the above interactions.

- Overall Methodology

  The pollutants most needing control need to be identified, either because of the quantities emitted or their toxicities, or both. Decision criteria are needed to determine the relative priorities to be assigned to controlling specific pollutants.

  The environmental assessments to be performed will require quantitative emission and distribution data for specific coal cleaning plant configurations, coal types, geographic locations, etc. In developing and illustrating assessment criteria and methodologies, this study utilizes approximations of emissions and dilutions such as might be associated with a hypothetical coal cleaning plant.

- Physical Transport and Partition Functions

  Estimates of environmental concentrations of pollutants in all three media - air, water, and land - are needed. This estimation initially involves physical transport and dispersion; the approaches to modeling physical distribution are discussed.

- Biological Transport Within Ecological Systems

  Ecological transport and distribution has not been adequately investigated; there are large gaps in the data for many elements and many species. Qualitatively, the pathways and mechanisms for dispersion, accumulation, and magnification have been identified;

the problems arise in attempts to quantify the rates of movement based on these mechanisms. The approach to these problems and several illustrative examples are described.

- Establishing Goals Based on Estimated Permissible Concentrations (EPC's)

  One of the most critical information needs is dose-response data on the health and ecological effects of individual pollutants and their mixtures. Then, estimated permissible concentrations (EPC's) can be derived. Also needed are improved methods for converting toxicological data to the threshold effects levels represented by EPC's, and biologically supported safety factors for incorporation into the formulae. The complexities of deriving EPC's on the basis of available toxicological data are discussed.

INTRODUCTION

As increasing reliance is placed upon coal as an energy source, the need to minimize the environmental impacts resulting from pollutant emissions will become more and more important. Recognizing this need, the U.S. EPA has initiated a number of programs to (1) assess the environmental impacts of fossil fuel energy processes and (2) identify problem areas requiring further research and development. Battelle-Columbus has been investigating the environmental assessment of coal cleaning processes since the fall of 1976. The following describe some of the activities in the area of development of assessment methodology and assessment criteria, including decision criteria to determine the relative priorities to be assigned to controlling specific pollutants so that attention can be focused on those most needing it.

A fundamental criterion for assessing the environmental impacts of pollutants associated with coal cleaning is the relationship of the permissible environmental concentrations of pollutants to those which can or do occur. Elucidating this relationship involves four interrelated activities illustrated by Figure 1. The first step is documentation of chemical characteristics of the waste streams with the physical transport and distribution characteristics of the pollutants of concern in air, water, and on land being the next step. This is then followed by estimations of the biological transport of those pollutants within the ecosystem where the pollutants may reach any number of receptor organisms, including man. The fourth activity estimates health and ecological effects relative to the dosages predicted by the above interactions. All four activities provide input for a prioritization of pollutants.

WASTE STREAM CHARACTERIZATION

The pollutants which most need control, either because of the quantities emitted or their toxicities, or both, need to be identified. The pollutants directly resulting from coal cleaning are primarily inorganic compounds associated with the ash fraction; water will be the major receptor of these pollutants. Operations producing major emissions of air pollutants are infrequent in coal cleaning. The largest air emissions will arise as particulates from thermal dryers and as fugitive dust from coal storage and refuse piles and from coal handling.

Data from the U.S. Bureau of Mines, the U.S. Geological Survey, and other sources were utilized to develop lists of potential

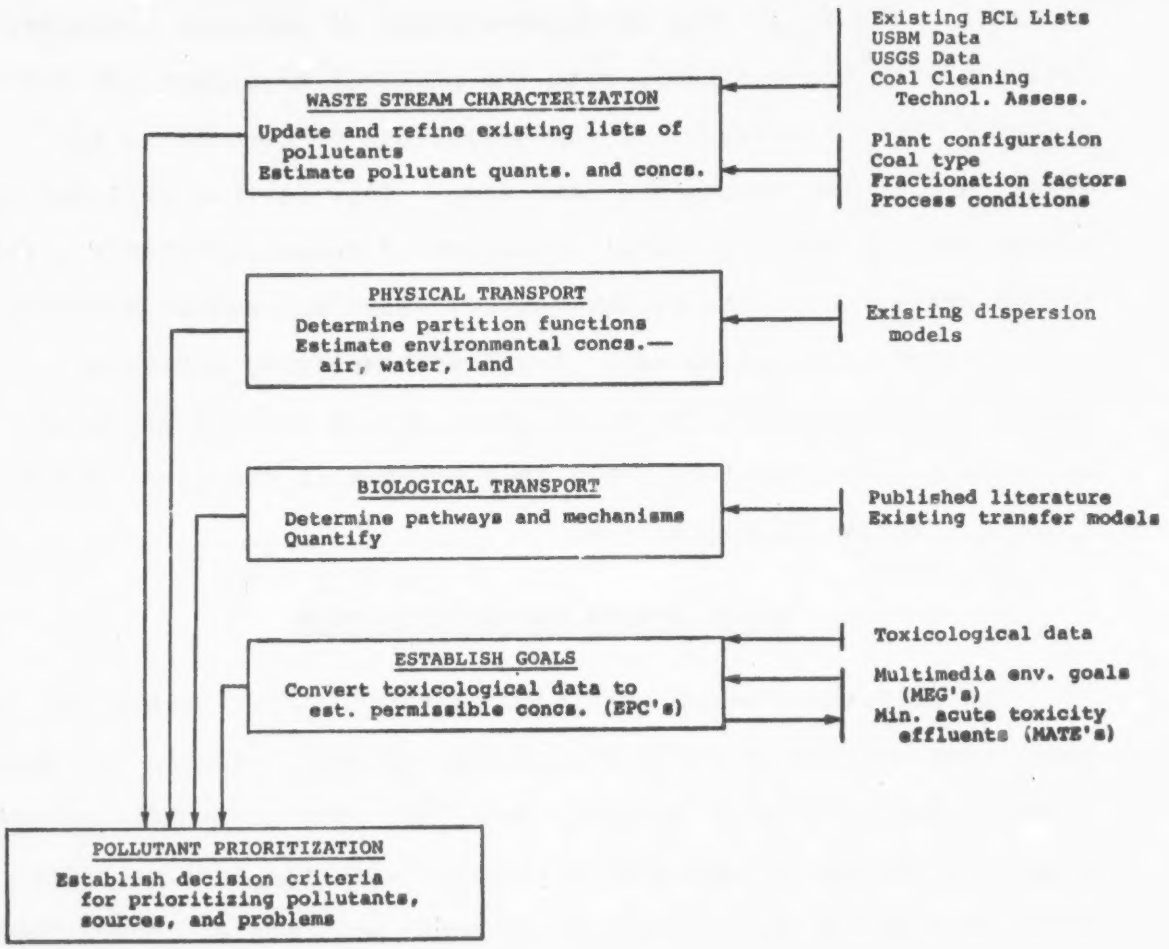

WASTE STREAM CHARACTERIZATION
Update and refine existing lists of pollutants
Estimate pollutant quants. and concs.
Existing BCL Lists
USBM Data
USGS Data
Coal Cleaning Technol. Assess.
Plant configuration
Coal type
Fractionation factors
Process conditions
PHYSICAL TRANSPORT
Determine partition functions
Estimate environmental concs.— air, water, land
Existing dispersion models
BIOLOGICAL TRANSPORT
Determine pathways and mechanisms
Quantify
Published literature
Existing transfer models
ESTABLISH GOALS
Convert toxicological data to est. permissible concs. (EPC's)
Toxicological data
Multimedia env. goals (MEG's)
Min. acute toxicity effluents (MATE's)
POLLUTANT PRIORITIZATION
Establish decision criteria for prioritizing pollutants, sources, and problems

Figure 1. Environmental assessment scheme.

pollutants of concern. Such lists tend to become inordinately long, if large doses of judgment are not used. Thus, a selected "Priority 1" list of 51 elements and 23 substances or groups of substances was selected judgmentally from larger lists for investigation (Battelle, 1977). The need for further pruning and prioritization of pollutants will be discussed later. The waste streams need also to be characterized as to pollutant quantities and concentrations to provide the data needed to estimate environmental concentrations. Pollutant emissions are dependent on a number of governing factors, including coal types, fractionation factors, process conditions, and geographic location. Ultimately, these data will come from specific measurements; but in the interim, these have to be estimated.

The various lists of potential pollutants identify those pollutants which may be of concern in coal cleaning, provided that they are present and emitted above some yet undefined rate of release and/or concentration. By virtue of its origin, coal has been found to contain nearly every naturally-occurring element. The concentrations of these elements in coal vary widely. Many of these elements, e.g., arsenic, beryllium, cadmium, lead, and mercury are recognized as toxic substances. The ranges of pollutant concentrations characteristic of coals provide some information on their presence, but none on their possible emissions. Input data required to estimate emissions include, first, information on the process steps embodied in the cleaning flowsheet. Many alternatives and combinations of alternatives are possible in crushing, sizing, and washing coal, and in separating coal from refuse. The actual combination of process elements will influence the degree of pollutant emissions, but not the kind. Thus, for purposes of developing assessment criteria and methodology, reasonable approximations of a generic process flowsheet will suffice, and are used in this discussion.

The second item needed for the estimation of emissions is information on partitioning of the pollutants or "fractionation factors", i.e., the distribution of substances in raw coal to another fraction or phase as the coal passes each process step. Generally, data are needed for each pollutant which give the fraction of the pollutant in the raw coal which distributes to the refuse, clean coal, bottom ash, fly ash, and the atmosphere.

Estimates of the distribution of elements between clean coal and refuse can be developed using float-sink or "washability" data, which have been determined experimentally for many coals. Gluskoter et al. (1977) have intensively examined this aspect of coal cleaning, concentrating on Illinois Basin coals, but also including other eastern coals.

If it is desired to base the calculations on a specific coal, for which washability data are available, fractionation factors calculated for that coal can be used. A simple computer program has been developed and tested which permits estimation of fractionation factors for elements as a function of specific gravity cutoff points and/or percentage yield.

"Fractionation factors" are also available from Klein, et al. (1975) and others for the partitioning of elements upon combustion in a boiler. These can be used to estimate losses to the atmosphere from the thermal drying of cleaned coal. For partitioning of elements between coal and the atmosphere during transporting, handling, and storage, "fractionation factors" would correspond to emission factors, such as have been estimated by the U.S. EPA (1973) and others, for example (Blackwood and Wachter, 1977). Analogous "emission factors" have yet to be developed for losses of pollutants leached out from coal storage piles, ash ponds, etc.

Values of emission concentrations are required as input to dispersion models to permit the calculation of ground level concentrations (GLC) for air pollutants and surface water concentrations (SWC) for water pollutants. A simplified preliminary material balance model has been developed covering the direct process steps from raw coal to combusted ash, illustrated by Figure 2. The incidental losses to air and water arising from transportation, handling, and storage are not included in this preliminary model, but can readily be included when data become available. The model, which is normalized to a combustion output of 10^6 Btu, can provide estimates of absolute emissions and average concentrations of any number of trace constituents in (1) refuse, (2) thermal dryer atmospheric discharge, (3) stack discharge from combustion, and (4) ash flow based on composite flows, given an analysis for the starting raw coal.

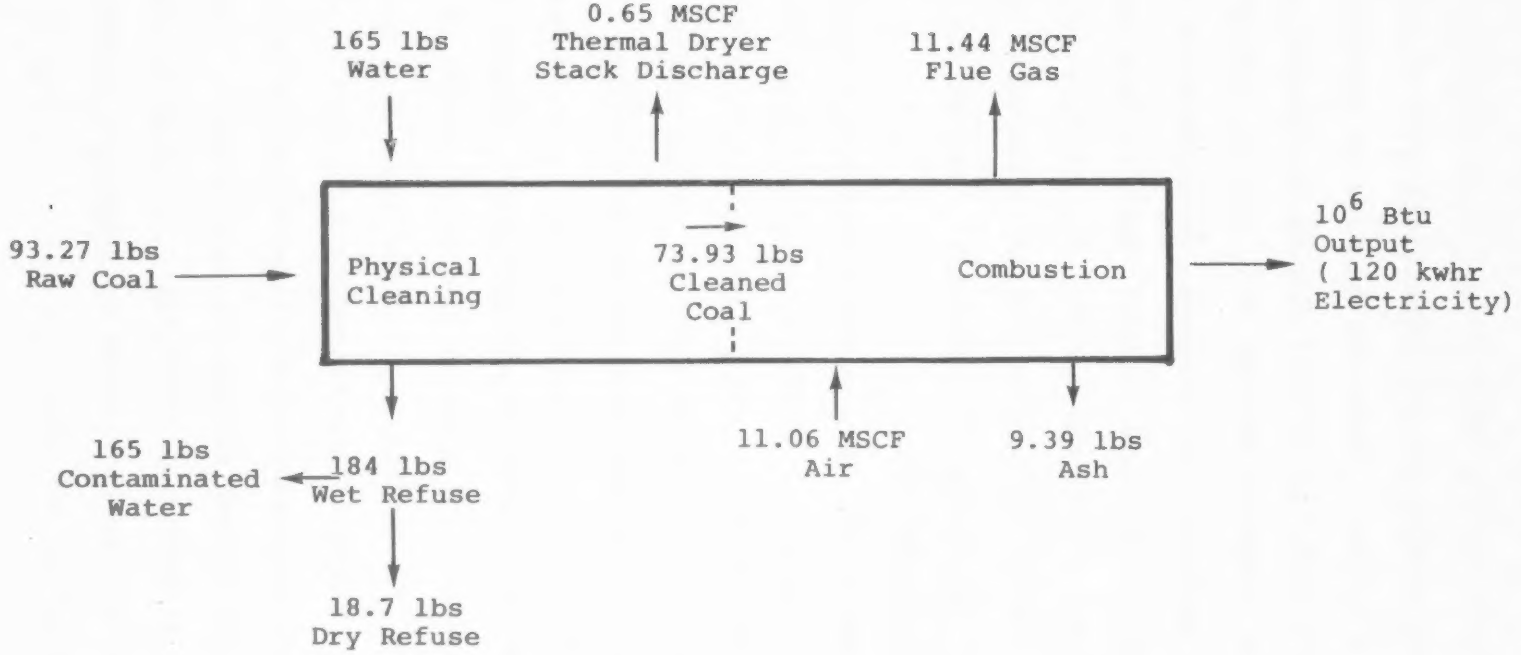


Figure 2. Flow quantities for coal cleaning/power plant complex

The model has been derived, programmed, and run with example cases, using a composite fuel analysis of 68 percent coal from the Helvetia mine and 32 percent from the Helen mine, approximating one possible coal feed, to the Homer City advanced coal cleaning facility.

PHYSICAL TRANSPORT

Pollutants emitted in the course of coal cleaning, handling, transportation, storage, and combustion can both accumulate and disperse, in both a physical and biological sense, depending upon the characteristics of the pollutant and the compartment. Biological transport and fate are discussed in the following section. In this section, modeling of the preceding physical transport and dispersion are discussed. The general need for modeling is to make estimates of the concentrations of trace pollutants in environmental media as a result of operation of a coal cleaning plant. No regulations or design criteria are available yet for most of these, although regulations will be proposed and promulgated by EPA within the next year or two for a number of toxic pollutants which may affect coal cleaning plants.

In succeeding paragraphs, modeling approaches are discussed relative to surface water, groundwater, air, and porous media. Generally, the air pollution model should account for deposition, both wet and dry, providing one input to surface water and soils. Surface water run-off will pick up material in the upper soil layer. The coal pile will be leached from precipitation and also generally carried into surface water. Leaching and leakage through sedimentation pond bottoms will generally contribute to groundwater pollution, although the movement of some pollutants through the subsoil and into the groundwater requires years because of adsorption of materials on soils. The refuse area, usually some kind of a fill, will be leached by the downflow of water from precipitation and surface flow, contributing to both stream pollution and groundwater pollution. The rationale that should be incorporated in the modeling approach is to build a capability of evaluating individual coal cleaning complexes, either existing or under design. This approach is recommended because the many different characteristics, e.g., meteorology, topography, stream geometry, soil, and groundwater characteristics required to characterize a given complex, vary widely from one plant to another, making generalizations risky at this time.

On the other hand, the objective of the present investigation is to develop criteria and associated methodologies for their application rather than to estimate site-specific environmental impacts for a given complex. The solution would seem to be to include the necessary provisions in the models for the multiplicity of detailed parameters which will ultimately be required, but to use nominal values, or ranges, or even possibly "worst-case" estimates, for a hypothetical site in the developmental phase.

Validation is an important aspect of model development, and should be planned for, utilizing one of the coal cleaning sites chosen for field data acquisition. Field data will permit validation and calibration of the models and suggest their application for future sites. However, it is not possible within the time frame of the present program to wait until field data are available to initiate model development. For that matter, it is not desirable to wait because modeling will illustrate the required data which need to be gathered and will give preliminary evaluations, using data that are available in the literature from other area.

Air Dispersion of Pollutants

The concentration of key pollutants in the thermal dryer atmospheric discharge and in the flue gases from combustion of the cleaned coal will provide input for calculations of atmospheric dispersion to yield ground level concentrations. The basic purpose of the dispersion calculation is to provide an estimate of the dilution factor which, when divided into the stack emission concentrations, will yield ground level concentrations.

Two basic models are required, depending on whether the pollutant is associated with large or small particles, where 100 microns is a typical dividing point. Large particles tend to deposit on surfaces close-in such that the air concentration is depleted as distance from the stack increases. The concentration of smaller particles is reduced only by dispersion.

Simplified dispersion models, as typified by that presented by Turner (1970), are availabe to consider stack heights and diameter, stack gas temperature and exit velocity, and ambient air temperature and wind speed. Calculations would be performed for different weather categories. Multiple sources can be considered to include the effects of more than one stack if distance between stacks is large enough to merit this refinement.

The large particle deposition model requires only the deposition factor, wind speed, and effective stack height. Deposition factors are available in the literature for various wind speeds of interest.

A fugitive dust emission model, based on the EPA Multiple Point Source Model (PTMTP), has been used by Battelle to help in selecting sampling sites at the Homer City coal cleaning plant, and to project mass atmospheric concentrations. It is a Gaussian plume, multiple source model, with a generation function for fugitive emissions dependent on wind speed squared. Deposition is accounted for (but not plume depletion). The model has been calibrated based on field data acquired at Homer City (Ambrose et al., 1977).

Water Dispersion of Pollutants

Two types of effects may need consideration for discharges of pollutants to water: dispersion and sedimentation of particulate solids, and dispersion and dilution of soluble pollutants.

For the estimation of surface water concentrations, the concentrations of pollutants and the flows of waste water discharges are required as input. Emission sources to be considered include the waste water discharge from coal cleaning and runoff and percolation from coal and refuse storage piles, as well as from ash ponds at coal cleaning plants and from coal storage piles at user plants.

Sedimentation in settling basins can be modeled by the use of deposition coefficients. Since sedimentation requires only a portion of the pollutant from a water column, a residual concentration remains which is then further diluted by dispersion and additional sedimentation in streams, etc. Simplified dispersion models using point sources of pollutants can be used. These models provide a correlation of dispersion coefficient with flow velocity and stream configuration so that reasonable approximations for surface water concentrations associated either with a specific facility or with a generalized case can be calculated for average flows, low flows, and high flows. Sedimentation is incorporated by the use of deposition factors relating sedimentation rate to concentration of the pollutant in the water body. Output will consist of sedimentation rate and concentration in water as a function of position (normally distance downstream) for each case. Pseudo-steady state models are believed to be adequate. With these models, when a change of conditions is encountered such as a change of release rates or an increase in flow of the stream, concentrations make a step change from one steady state to another. Sediment accumulates on the stream bottom linearly with time until such a change in conditions occurs. Fully mixed (with stream across section and depth) models are more appropriate for small narrow streams which are likely to be around a coal cleaning plant. These solutions to the transport equation have been known for years, and they are reasonably applicable for continuously flowing freshwater streams.

The need for a sedimentation model is not certain. The U.S. Environmental Protection Agency has promulgated effluent guidelines for existing coal preparation plants and associated areas (U.S. EPA, 1977a), and also has proposed new source performance standards (U.S. EPA, 1977b), both of which establish upper limits of total suspended solids (TSS) of 70 mg/l (maximum for any one day) and 35 mg/l (average of daily values for 30 consecutive days). For new sources these values apply to facilities which recycle waste water for use in processing (nearly all new facilities should fall into this category). A no discharge of process waste water limitation is proposed for new facilities which do not recycle waste water.

The definition of "coal preparation plant associated areas" is broad, including plant yards, immediate access roads, slurry ponds, drainage ponds, coal refuse piles, and coal storage piles and facilities (U.S. EPA, 1977a). Thus, in order to be in compliance, effluent from all areas of a coal preparation plant, including coal and refuse piles, will have to be controlled so that the total aqueous TSS discharge does not exceed an average of 35 mg/l. At this concentration, sedimentation probably can be neglected.

Dispersion Through Porous Media

Although emission of pollutants to the atmosphere and to surface waters is regulated by the U.S. EPA, heretofore the invisible and difficult-to-measure escape of aqueous pollutants downward through the soil has essentially avoided regulation. This situation is beginning to change, and this pollutant transport path should be considered in regard to environmental criteria for coal cleaning plants. As mentioned in the introduction to this section, this pollutant release pathway can come into play beneath storage piles of raw and cleaned coal or refuse, as well as under refuse ponds.

Simplified approaches to the adsorption and leaching of pollutants in porous media are available. Simplified one-dimensional models are described by Raines (1966) along with comparisons with sophisticated results such as computerized finite difference models with Langmuir adsorption-desorption. In many cases the simplified models are quite adequate. It is recommended that initial emphasis can be directed toward correlation of data and estimation with these models.

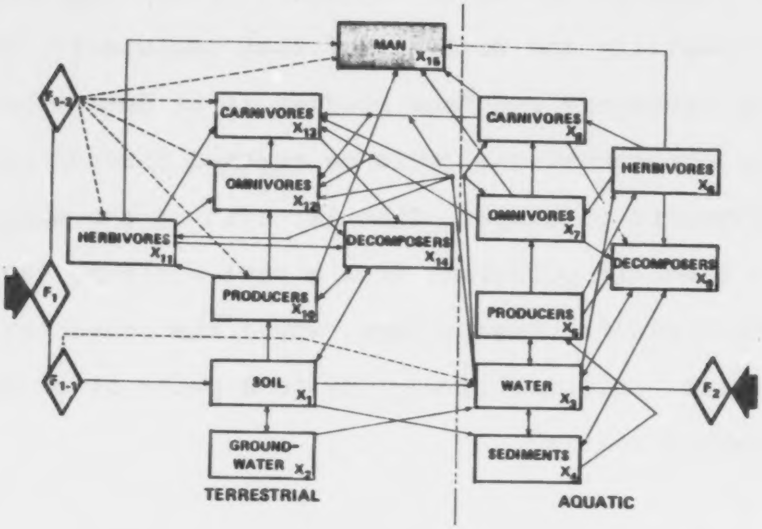
Groundwater modeling for accurate estimation of flows and resulting trace contamination is sophisticated and complicated. A sophisticated approach is not deemed within the scope of this program at the present time. Socme experimental data are available for various trace elements and various soils.

ECOLOGICAL TRANSPORT

Coal cleaning facilities have a number of potential sources of pollutants which include leachate and runoff from coal storage and refuse disposal piles, process wastewater or blowdown from closed water circuits, and dust and gases emitted from coal piles, refuse piles and thermal dryers. The more apparent environmental effects from these potential contaminants might be seen in direct contact toxicity resulting from changes in pH in the surrounding media, increasing levels of sulfate sulfur, sulfur dioxide, nitrate nitrogen and nitrogen oxides, or resultant chemical changes in abiotic components. These types of effects are usuaally short-term and easily identified. But, what happens to those trace elements (e.g., arsenic, cadmium, and mercury) whose release into both terrestrial and aquatic ecosystems is not quite so apparent?

This portion of the environmental assessment criteria study has focused on a short list of potentially hazardous trace contaminants that might be released as a result of coal cleaning. These include elemental, inorganic, and organic forms of: arsenic, beryllium, cadmium, iron, lead, manganese, mercury, and selenium. It is well known and documented that these contaminants are absorbed, retained, released, and cycled among the biotic (i.e., producers, herbivores, omnivores, carnivores, and decomposers) and the abiotic (i.e., soil, groundwater, surface water, and sediment) compartments (see Jackson and Watson, 1977; Jackson et al., 1978; Huckabee and Blaylock, 1974; Friberg et al., 1974; D'Itri, 1972; and Van Hook et al., 1974). The structure and complexity of transfer pathways and the matrix notation of the typical ecosystems in question are depicted in Figure 2. For the purpose of this paper, cadmium and mercury are used as examples of the types of information that are available in Ewing et al., 1978.

The toxicity of these contaminants to living systems under certain conditions has been established by other researchers (Luckey et al., 1975). In addition, biotransformation of some



[F_1 (having components F_{1-1} and F_{1-2}) = airborne atmospheric forcing function, and F_2 = aquatic input forcing function.]

			Abiotic Components				Aquatic Components					Terrestrial Components					MAN
			Physical Transport				Biological Transport										
			X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	X_{10}	X_{11}	X_{12}	X_{13}	X_{14}	X_{15}
Physical Transport	Abiotic Components	Soil X_1		●	(b)											●	
		Groundwater X_2	●														
		Surface Water X_3	●	●		●					●						
		Sediments X_4			●						●						
Biological Transport	Aquatic Components	Producers X_5			●	●											
		Herbivores X_6			●	(a)	●										
		Omnivores X_7			●	(a)	●	●									
		Carnivores X_8			●	(a)		●	●								
		Decomposers X_9			●	●	●	●	●	●							
	Terrestrial Components	Producers X_{10}	●													●	
		Herbivores X_{11}	(a)		(c)							●					
		Omnivores X_{12}	(a)		(c)			●	●	●		●	●				
		Carnivores X_{13}	(a)		(c)			●	●	●			●	●			
		Decomposers X_{14}	●									●	●	●	●		
		MAN X_{15}		(d)	(d)			●	●	●		●	●				

(a) Indirect ingestion resulting from feeding habits.
(b) Irrigation, nominal in areas of groundwater irrigation.
(c) Surface water intake.
(d) Drinking water intake.
● Dominant system transfer.

(The matrix is defined so that the column element is the donor compartment and the row element is the recipient.)

(Man is shown, but no data are reported.)

Figure 3. Compartmental model of generic ecosystem and dominant pathways of pollutant transport and matrix configuration of important rate transfer coefficients within the generic ecosystem.

contaminants (i.e., mercury), as shown in Figure 4, can drastically change both the availability and toxicity of that pollutant. So, the ultimate goal of transport and fate studies is to determine whether or not toxic concentrations could be reached through normal environmental exposure pathways. That is, even if the source release rates for a specific pollutant from a coal cleaning facility were below the current Federal regulations, would the concentration of the contaminant ecologically magnify to a point at or beyond the toxic threshold values?

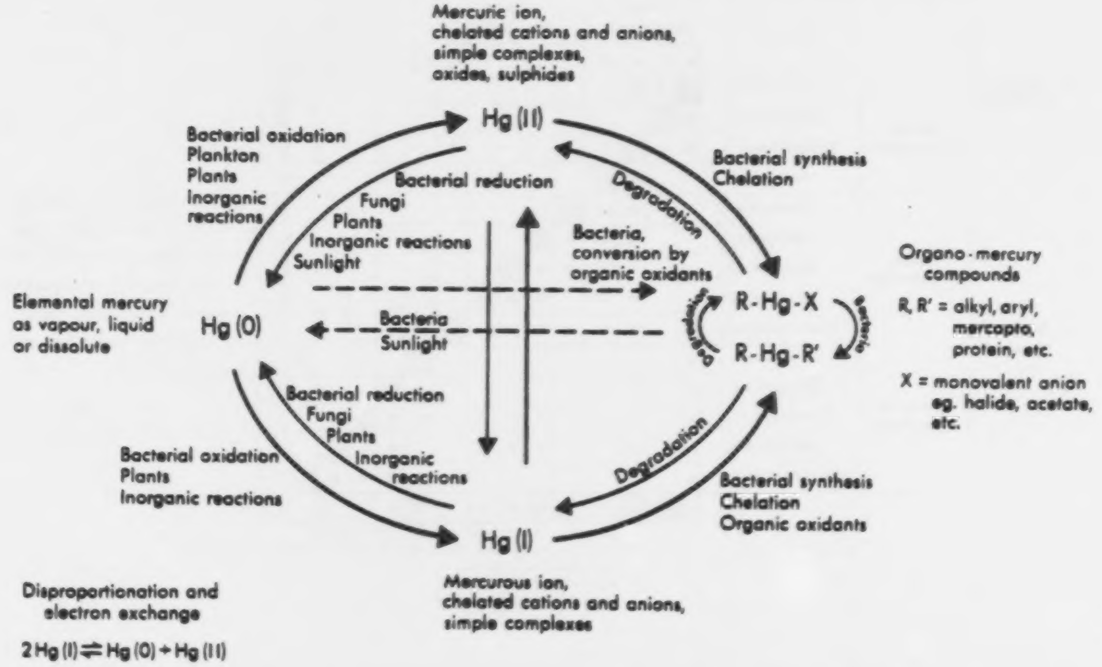


Figure 4. Cycling of mercury interconversions in nature (with permission from I. R. Jonasson and R. W. Boyle, 1971).

When magnified by an organism, concentration of a contaminant on a per gram basis is greater than that of its source or donor compartments. The term describing this is ecomagnification which is non-source specific and includes all potential exposure pathways (ingestion, inhalation, adsorption and immersion) within the ecosystem. Ecomagnification is frequently misunderstood as a simplistic biological phenomenon when, in fact, it is quite complex. Ecomagnification is all inclusive, whereas the classic term biomagnification only considers food ingestion as the mode of exposure. Thus, the ability of an organism to accumulate or magnify contaminants depends on a number of ecological, chemical, physiological, and physico-chemical factors, such as:

- chemical form of contaminant
- concentration of contaminant in soil or water
- interaction with other trace elements
- biotransformation of original elemental form
- soil characteristics and properties
- physiological makeup of target organism
- complexity of food sources.

In this study, the concentration factors (i.e., percent uptake or retention) for the pollutants investigated have been extracted from the available literature for the major ecosystem compartments shown in Figure 3 (see page 16). Tables 1 and 2 present typical data entries for cadmium in the terrestrial ecosystem and mercury in the aquatic ecosystem. Data on cadmium and mercury were selected because they are the most complete of all the pollutants

Table 1. Cadmium uptake

Sample	Source Form	Percent Uptake/Retention (concentration basis)	Reference
		Abiotic Components	
Soil	$^{109}CdCl_2$ in simulated rain $^{115}CdCl_2$ in simulated rain $CdCl_2$ in simulated rain	98.9 ± 1.2 85.5 88.4 ± 2.7	Van Hook et al., 1974 Huckabee and Blaylock, 1974 Van Voris et al., 1978
		Terrestrial Producers	
Vegetable Crop	Cd in soil	141.26 ± 24.0	Ratsch, 1974
Oak Trees	Cd in litter-soil	34.9 ± 0.5	Jackson and Watson, 1977
		Terrestrial Herbivores	
Rabbit	Cd iron dust	~30	Friberg, 1950
Cow	$CdCl_2$ in feed	8	Miller et al., 1967
Grasshopper	Cd in vegetation	~130	Munshower, 1972
		Terrestrial Omnivores	
Chipping Sparrow	Wild bird seed soaked in ^{109}Cd solution	8	Anderson and Van Hook, 1973
Field Cricket	Vegetation grown in ^{109}Cd solution	60.9	Van Hook and Yates, 1975
		Terrestrial Carnivores	
Dog	$CdCl_2$ in gaseous form	~40	Harrison et al., 1947
Wolfe Spider	Crickets fed on ^{109}Cd-grown vegetation	71.4	Van Hook and Yates, 1975
Predatory Arthropod	Cd in prey	124.0 ± 93.5	Watson et al., 1976
		Terrestrial Decomposers	
Earthworm	Cd in soil	$1.74 \times 10^3 \pm 0.42 \times 10^3$ $1.03 \times 10^3 \pm 0.03 \times 10^3$	Van Hook et al., 1974 Gish and Christensen, 1973
Woodlouse	Cd in litter-soil	$8.96 \times 10^2 \pm 1.90 \times 10^2$	Martin et al., 1976
Arthropod litter consumer	Cd in litter	36.8 ± 18.4	Watson et al., 1976

Table 2. Mercury uptake

Sample	Source Form	Percent Uptake/Retention (concentration basis)	Reference
		Aquatic Producers	
Rooted Plant (*Elodea densa*)	$CH_3{}^{203}HgCl$ and $^{203}HgCl_2$ solution	$5.19 \times 10^6 \pm 3.35 \times 10^6$	Mortimer and Kudo, 1975
Water milfoil (*Myriophyllum specatum specatum* L.)	organic and inorganic Hg in solution	$2.21 \times 10^4 \pm 1.76 \times 10^4$	Dolar et al., 1971
		Aquatic Omnivores	
Goldfish (*Carassius auratus*)	$HgCl_2$ in solution	$1.14 \times 10^4 \pm 1.03 \times 10^4$	McKone et al., 1971
Snail	^{203}Hg-tagged fly ash	0.13	Huckabee and Blaylock, 1974
		Aquatic Carnivores	
Fish (*Gambusia affinis*)	^{203}Hg-tagged fly ash Hg^0 and $HgCl_2$ in solution	0.02 2.1×10^4	Huckabee and Blaylock, 1974 Schindler et al., 1977

investigated. However, similar though less complete, data entries are available for each of the other six pollutants investigated for both terrestrial and aquatic ecosystem compartments (Ewing et al., 1978).

The ultimate goal was to identify likely distribution factors and supply much needed input data for simulation models describing the transport and fate of these pollutants. The computer simulation of transport and fate would enable scientists to compare the computer-predicted, long-term body burdens with reported toxic concentrations for each of the pollutants. As is evidenced in Tables 1 and 2 (pages 19 and 20) there are some indications that both cadmium and mercury have the propensity to ecomagnify. However, the data are extremely variable and depend on the above listed (see page 18) influencing factors. Unfortunately, the need to use computer simulations and then compare the results to reported toxic effects values is currently ahead of the data base. The data required to accurately calculate the rate transfer coefficients currently are not available in the literature. Investigators, in general, fail to consider or report: (1) the measurement of major parameters affecting transport and fate, (2) partitioning data into specific exposure sources (i.e., food source, inhalation, direct absorption), (3) chemical form of the pollutant, and/or (4) time duration of the experiment. Therefore, the use of computer modeling to accurately predict ecological transport and fate of pollutants is currently beyond the state-of-the-art.

The resulting recommendations for future research fall into three major categories. First, there is an immediate need to conduct research designed to determine the relative importance of each exposure pathway for a series of populations within each compartment. A series of closely controlled experiments could be designed to estimate these values. This would enable concentrated effort to be focused on the second major category which is the determination of the rate transfer coefficients for chemical forms for each dominant pathway. The third category of recommended research is simulation model development and field test validation of the forecasts obtained from such models. An orderly timing of these research recommendations could produce an accurate, short-term index of anticipated impact from released trace contaminants from a coal cleaning facility for the environmental assessment program.

ESTIMATION AND RATIONALIZATION OF BIOLOGICAL EFFECTS

Many species of plants, animals (including man), and microorganisms will be found living near coal cleaning facilities. Many individuals will be exposed to pollutants from the facilities' emission streams. If pollutants are discharged to the atmosphere, toxic materials may be transported, as indicated earlier, and be breathed by animals and plants. Waterborne chemicals can be transported and later affect aquatic plants, animals, and microorganisms. Nondegradable pollutants can be leached from landfilled materials and be taken up by crop species to man as well as other receptor organisms and enter food chains. Previous sections have dealt with our knowledge of such transfers for the short list of priority pollutants. However, exposure alone does not assure an effect. Thus, the problem becomes one of determining if a specified concentration of pollutants can harm living organisms in a measurable and significant way once transferred to the organisms.

Documenting and evaluating biological effects ideally should precede setting of environmental goals and development of control technology for coal cleaning facilities. The burden of proof for establishing environmental goals rests with health and ecological effects data; i.e., if no problem exists, there is no need for a solution. Data need to be sound, complete, rigorous, and they must be interpreted correctly to support environmental goals and recommendations for further development of control devices for coal cleaning facilities. More details on this point and the types of biological effects are found in Cornaby et al., 1978. Unfortunately, biological effects data are not only relatively sparse compared to those needed for adequate assessments but also are typically laboratory results rather than real results from practice. Thus, the following material was developed as another step in providing the necessary feedback for prioritizing pollutants for purposes of control strategies, i.e., which substances need how much control in order to protect human health, non-human populations, and ecological systems.

Most biological effects data are obtained in the laboratory and need to be extrapolated to "real world" situations. Extrapolation is the process of inferring or extending a known toxicological response into an unknown area. Conjectural knowledge of the unknown area is developed based on assumed continuity, correspondence, or other parallelism between it and what is known. Often, biological effects need to be extrapolated from (1) laboratory to field—many differences, including lack of transfer coefficients, make this difficult, (2) one species to another—no two species are alike, (3) one medium to another—drinking is not the same as breathing, and (4) one life stage to another—ranges of sensitivity may differ by four orders of magnitude. In practice, biological effects data are collected from a few life stages of a few species for a few routes of entry in a few controlled conditions. On the other hand, the real world situation around a coal cleaning facility contains thousands of species in many stages of growth, all of which may be continuously exposed to various types of doses. Extrapolation is almost as much an art as a science; almost everyone is aware of this. Clearly, extrapolation must be done with caution.

Despite the technical difficulties involved in estimating permissible concentrations of toxicants to organisms, approaches are available for dealing with the problem. There are formulae--some of them developed by or for the U.S. EPA (Handy and Schindler, 1975). The formulae have two basic parts: a dose/response part and an adjustments part. The dose/response generally consists of one of the typical laboratory effects measurements: LD_{50}, LD_{LO}, and TL_m-96 hr*. Each effects measurement is adjusted by several factors—the argument being that the adjusted dose/response data better conform to the "real world" situation. Adjustments include the following media conversion (e.g., airborne to waterborne toxicants), safety factors (e.g., 0.01), various types of exposure (e.g., workday to full week), and elimination rate (e.g., biological half-life).

The Multimedia Environmental Goals (MEG) chart is the principal tool for displaying goals developed with the use of formulae. The chart was developed at EPA's Industrial Environmental Research Laboratory (IERL) and has been refined by Research Triangle Institute (RTI) (Cleland and Kingsbury, 1977) with some assistance from Battelle's Columbus Laboratories. The chart consists of two interrelated tables: (1) a control engineering part including columns for best technology and minimum acute toxicity effluents (MATE's) and (2) a health/ecological part including columns for standards/criteria for both human health and ecological systems. The chart has rows for the three media--air, water, and land. The MEG chart is considered an indispensible part of the Environmental Assessment programs at IERL. Any work on the development of environmental goals needs to be applicable, eventually, to MEG chart activities. Applications of currently available values are presented in the paper by Tolle et al. (1978, conference proceedings). In the present section, the thrust of the research is to expand and improve the quality of the current environmental goals.

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*LD_{50}: Lethal dose 50, i.e., the dose of a pollutant required to kill 50 percent of a particular animal species by methods other than inhalation.

LD_{LO}: Lethal dose low, i.e., the lowest dose of a substance introduced in one or more portions by any route other than inhalation over any period of time and reported to have caused death in a particular animal species.

TL_m: Median tolerance limit value, i.e., the concentration in water of a pollutant required to kill 50 percent of a particular aquatic species.

The major strengths and limitations of some 20 formulae currently in use were identified. Extrapolation formulae were reviewed from three viewpoints: media, dose/response data, and adjustment factors. This evaluation led to improvements in the state-of-the-art for estimating biological effects.

Ten major strengths of the formulae were identified. Some of the most powerful were embodied in the formulae used to estimate permissible concentrations for airborne pollutants. These formulae use a variety of the most rigorous dose/response data which include a variety of measurements, e.g., threshold limit values (TLV's) and other large data sets. The ability to incorporate simple adjustment factors is seen as a strength; generally, the prediction is assumed to improve as more adjustment factors are incorporated. Particularly useful adjustment factors are those for exposure time, elimination rates, and safety factors.

Seventeen major limitations of the formulae were identified. From the media viewpoint, the formulae for land- or food-borne pollutants exhibit the most limitations; the crop uptake model is too simplistic, among other deficiencies. Many available toxicological response data, e.g., LD_{LO}'s, have not been used in the available formulae. Responses are limited to a few species of animals; few or no responses are provided for plants and microorganisms. The bulk of the effects data is based on acute or short-term exposure when chronic or long-term exposure effects data are needed. The effects data are for single chemicals when responses to mixtures of chemicals are needed. So, from the dose/response viewpoint, there are several limitations. From the adjustment factor viewpoint, there is a need for validation of the reasonableness of the factors. Safety factors need a biological basis. And, for every limitation in the effects data, there should be an attempt at a compensatory factor. Thus, if the chronic effects data are available, a chronic adjustment factor could help extend the acute effects data. In summary, there are many limitations.

Research concentrated on the reduction/removal of five of the limitations: identification of alternative state-of-the-art formulae, correlation of nonoral with or LD_{50}'s, use of chronic effects data, extrapolation of data from one species to another, and development of a biological basis for safety factors. The following material summarizes some of the major points and recommendations achieved in the research.

Alternative Formulae

Other formulae could be incorporated into the present system. Some formulae handle exposure and biological half-lifes more rigorously than any one of the 20 formulae. Typical state-of-the-art formulae are those for (1) maximum permissible concentration for radioisotopes (International Commission on Radiological Protection, 1959) and (2) CUMEX (cumulative exposure) index (Walsh et al., 1977). Inclusion of the former could provide a more rigorous estimation of waterborne radionuclides and related pollutants. The latter could provide estimates for air and water separately and simultaneously. Multiple exposures are the reality and more formulae, capable of handling such exposures, need to be developed for future estimations of potential dangers to living organisms.

Correlate Nonoral with Oral LD_{50}'s

One of the more quantitative formulae (Handy and Schindler, 1975) in use requires that dose/response data be in the form of oral LD_{50} for rats. However, there are many nonoral toxicological response data which could be used, if a conversion method were available. To overcome this limitation, specially designed equations were developed by Battelle's Columbus Laboratories to permit conversion of toxicological data for nonoral routes of administration to the oral route. Conversions were developed for intravenous, intraperitoneal, and subcutaneous LD_{50}'s and inhalation LC_{50} to the oral LD_{50}. For example, the relationship for intravenous LD_{50} to oral LD_{50} is:

$$\ln(\text{oral } LD_{50}) = -0.57 + 1.59 \ln(\text{intravenous } LD_{50}) \quad .$$

This research expands the access to other readily available toxicological effects data and is immediately applicable. This type of research needs to be extended to better utilize the wealth of toxicological data for other routes of administration, e.g., LD_{LO}, TD_{LO}, LC_{LO}, etc., and for other species (e.g., mice, hamsters and dogs).

Introduce Chronic Effects Data

Limitations inherent to biological effects data for short-term (acute) exposure can be removed only by use of effects data for long-term (chronic) exposure. Chronic exposure (low levels of chemicals for long periods of time) can depress reproductive capacity, increase the number of malignant tumors, and generally shorten the life span of males, females, or both. Chronic effects for life-term (1000+ days) and multigeneration (three-generation) studies for rodents were examined; Table 3 provides such data. It is assumed that concentrations lower than those used in acute exposure (high levels of chemicals for short periods of time) cause effects that could not have been known on the basis of acute tests only. Concentrations of 5 ppm for some elements in drinking water seem to show increasingly harmful effects the longer the study and the greater the number of generations studied. At present, there seems to be no quantitative way to predict chronic effects based on effects data only from acute experiments. When chronic effects data are available, they should be used in the

Table 3. Selected chronic effects on multigenerations of rodents of selected pollutants

Element	Water Dosage (ppm)	Effects
Control	—	Death and runts rare; bred normally for 4 years
As	3	Mice survived well thru F_3; reduction in litter size
Cd	10	Toxic to breeders by F_2; 13 percent runts
Ni	5	Litter size decreased; few males in F_3
Se	3	Strain began to die by F_3; 24 percent runts

Source: Schroeder and Mitchener, 1971.

F_2 = second filial generation.

F_3 = third filial generation.

dose/response part of the formulae if the effects are greater than those indicated by acute exposure data.

Extrapolation of Response from One Species to Another

Animal toxicity data can be extrapolated from one species to another in at least two ways. In one approach, the equation deals with only one toxicant at a time, but this single equation can be used to predict the responses of animals of many sizes (including man) to that particular toxicant. In another approach, the equation deals with responses to many different toxicants, but it can only be used to extrapolate from the response of one particular species to the response of another species (say, from rat to human). Both methods are related to the basic relationship of $Y = aW^b$ (Kleiber, 1947; Anderson and Weber, 1975) where Y = the response, W = body weight (or area), and a and b are constants relative to the particular Y. Unfortunately, the basic data are not readily available. Continued work in extrapolation of one species to another, especially man, is of such paramount importance.

Biological Bases for Safety Factors

The range of sensitivity for certain organisms to given toxicants provides a biological basis for safety factors. Toxic levels and effects of a substance vary greatly. For example, toxicity ratios for young of a species versus adults can vary from 0.002 to 16—a variation of nearly four orders of magnitude (Casarett and Doull, 1975). Green algae species differ in their response to cadmium by a factor of 100 (Buehler and Hirshfield, 1974). Frog embryos and larvae are more sensitive than adults to mercury by factors of 100 and 1000, respectively (Porter and Hakanson, 1976). Bird embryos and fetal and newborn mammals are more susceptible to metals than their adult counterparts (National Research Council, 1976). Baby mammals appear to be four to five times more sensitive than adults to some chemicals (Goldenthal, 1971). In aquatic situations, safety factors of 100 and 1000 seem reasonable if effects data are available from the most resistant species; if test data are for the most sensitive species, such high safety factors are unwarranted. In terrestrial situations, smaller safety factors seem biologically reasonable. For example, 10 to 100 would be reasonable when the available dose/response data are for resistant species.

All of these improvements still fall short of the needed advancements in this important research to protect human health and the environment from adverse effects. True, the formulae provide quantitative values and increasingly higher quality effects data and adjustment factors are being used in such formulae. The state-of-the-art predictions are not absolute; they are relative. Furthermore, the relative relationships of one prediction to another may not be correct. Caution is warranted. Validation and future monitoring are needed to confirm the reliability of the predictions. Another major step forward involves the issue of mixtures as compared to single chemical species. The approach of predicting permissible concentrations for single chemical species will need to be replaced by approaches addressing synergistic/antagonistic effects associated with the release and dispersion of actual emission streams. Then, establishing environmental goals and feedback to control technology development will be based, increasingly, on sound, complete, rigorous effects data.

Pollutant Prioritization

It is not difficult to generate a list containing 100 or more possible or potential pollutants which can result from coal cleaning; if coal utilization is included, the list can increase several-fold. Obviously, these are not all of equal importance. Thus, one of the goals of the coal cleaning environmental assessment program is to establish decision criteria to determine the relative priorities to be assigned to controlling specific pollutants.

As indicated in Figure 1 (see page 3) all of the environmental assessment subtasks shown provide input for a prioritization. Also, as noted earlier, a fundamental criterion for ranking the importance of any pollutant is the relationship between its expected environmental concentration and the maximum concentration which presents no hazard to man or biota on a continuous, long-term basis. The estimated environmental concentrations (EEC) of pollutants can be projected on the basis of coal feedstock, process configuration, control devices applied, environmental dilution and dispersion, etc.

The other half of the relationship, the estimated permissible concentration (EPC), is quite another matter. As indicated above, the toxicological and epidemiological data needed to characterize the relative health and ecological risks of the pollutants to be expected from coal cleaning processes are woefully inadequate. (The information base is in far better shape for many of the chemical compounds encountered in the chemical and similar industries, but almost none of these are of any concern to coal cleaning.) Additionally, the exact chemical form of many coal cleaning pollutants is unknown more often than not. There appears very little likelihood that the EPC data base for coal cleaning pollutants will improve dramatically in the near future.

Thus, in spite of its undeniable theorectical soundness and anticipated ultimate success, the EEC/EPC relationships will probably be unable to provide substantial prioritization guidance over the near term.

Looking toward the longer term, another of the U.S. EPA's contractors, the Research Triangle Institute, is developing the concept of multimedia environmental goals (MEG's) of which health-related and ecology-related estimated permissible concentrations of air, water, and land are key parameters. Current status of this ongoing effort has been described by Cleland and Kingsbury (1977). Because of the data insufficiencies mentioned above, the MEG tabulations for pollutants from coal cleaning processes are incomplete, which limits their present application.

Another approach to the estimation of acceptable concentrations utilizes Minimum Acute Toxicity Effluents (MATE's). These are considered to represent the very approximate concentrations of pollutants in air, water, and land effluents, below which only minimal harmful responses are evoked by short-term exposure. As reported by Cleland and Kingsbury (1977), six MATE concentrations may be described for a single compound with two MATE's based on health and ecology for each medium. While there are also large gaps in the toxicological data needed to estimate MATE's, the types of data from which MATE's can be derived are also of the short-term, acute category and are thus more amenable to empirical treatment.

Source Analysis Models (SAM's) have been developed by Acurex, another of U.S. EPA's contractors, to assist in comparing elements of an environmental assessment. The simplest SAM, designated SAM/IA, is designed for rapid screening of effluent streams and assumes no effluent transformation. As described by Schalit and Wolfe (1978), rapid screening of the degree of hazard and the rate of discharge of toxic pollutants may occur at any level of depth of chemical and physical analysis. In SAM/IA, effluent concentrations are compared to the appropriate MATE's; the comparison may also evaluate the difference between an uncontrolled process and one with pollution controls.

In the long run, a rigorous approach to the ranking of relative importance of pollutants will probably be possible. However, for the near term, utilizing the assumption that the relative importance of a pollutant can be based generally on its toxicity and its abundance and that those substances for which criteria have been established or which have been designated as pollutants are important. The preliminary "Priority 1" list of 74 pollutants mentioned earlier had its origin in these considerations. The relative importance of the 13 elements included in the "List of 65 Toxic Pollutants," recently published by EPA (43 FR 4108, January 31, 1978), has undoubtedly increased as a result of that listing.

Preliminary working prioritization lists can be derived by comparing the emission concentrations (uncontrolled and controlled) in each stream (air or water) with the concentrations established by air or water quality criteria or by regulation. These concentration levels may be health- or ecology-based, or both; or they may reflect available technology, e.g., "best available control technology" (BACT). Such lists will provide a working basis for prioritization of R & D efforts while the more precise and sophisticated MATE's and MEG's are being perfected. This is the direction of the current studies, and it is planned to develop a provisional pollutant rating within the next 6 months. This first generation prioritization will necessarily be based on less-than-rigorous criteria, including, where insufficient information is available, estimations based on scientific judgments. As more information is developed, refined lists will be generated.

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APPLICATION OF ENVIRONMENTAL ASSESSMENT METHODOLOGY TO HOMER CITY POWER COMPLEX BACKGROUND DATA: COMPARISON WITH MEG VALUES

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ABSTRACT

During the period from December 1976 through April 1977, a series of multimedia, grab-sampling campaigns were conducted by Battelle's Columbus Laboratories at the Homer City Generating Station near Homer City, Pennsylvania. The intent of this pre-operational monitoring was to document the abundance or concentrations of selected key parameters in order to evaluate the air, water, and biological quality in the vicinity of an advanced coal cleaning plant. These environmental studies, while not sufficiently long term to be a true baseline analysis, were conducted prior to operation of the cleaning plant as a reference point for future, and more comprehensive, environmental testing planned during operation of the plant.

The multimedia studies involved sampling, laboratory analysis, and evaluation of the following components of the environment in and around the Homer City Generating Station.

- Fugitive dust monitoring using high-volume samplers
- Water and stream sediment quality monitoring from grab samples
- Aquatic biota sampling of attached algae, bottom-dwelling invertebrates, and fish in streams
- Terrestrial biota reconnaissance of wildlife and vegetation within a two-mile radius
- Cleaning plant refuse disposal facility evaluation.

The objective of this paper is to present some of the fugitive dust, water, and sediment sample analysis data from the studies at Homer City and compare this data with the values listed in the Multimedia Environmental Goals (MEG) document prepared for the U.S. EPA by Research Triangle Institute. The MEG values considered in this paper are the maximum levels of significant contaminants that are judged to be appropriate for preventing certain negative effects in the surrounding populations or ecosystems. The MEG methodology

was developed to meet the need for a workable system of evaluating and ranking pollutants for the purpose of environmental assessment. The values considered in this paper include the following.

- Minimum Actue Toxicity Effluents (MATE's) - concentrations of pollutants in undiluted emission streams that are acceptable for short-term exposure.
- Estimated Permissible Concentrations (EPC's) - the maximum concentration of a pollutant which presents no hazard to man or biota on a continuous long-term basis.

The utility of the MEG approach to environmental assessment is explored in relation to the Homer City data.

INTRODUCTION

Battelle's Columbus Laboratories has contracted with the U.S. Environmental Protection Agency (U.S. EPA) to perform a comprehensive environmental assessment of physical and chemical coal cleaning processes. The broad goal of this program (Contract No. 68-02-2163) is to establish a strong base of engineering, ecological, pollution control, and cost data which can be used to determine those coal cleaning processes that are most acceptable from the technological, environmental, and economic viewpoints. The data base also will be used for pollution control trade-off studies that will compare the various individual and combination techniques for reduction of the pollution potential of coal-fired power plants. In addition, these data will be used to identify any areas where development of pollution control equipment may be needed.

Since one of the program goals involves an analysis of methods for reducing overall environmental pollution through the use of cleaned coal, mathematical and modeling techniques will be used for identification of optimum coal cleaning process configurations, pollution control equipment, and waste management techniques. These optimization studies will require an assessment of the pollution potential of coal cleaning processes, associated facilities, and--in certain cases--the end uses of coal.

In order to obtain the field data necessary for the overall program, Battelle is undertaking a sampling and analysis program designed to identify the combinations of coal cleaning processes and environmental conditions which are most effective in reducing the total impact of coal use on the environment. This will be accomplished through the characterization of process and effluent streams from a variety of coal cleaning facilities and their associated coal transportation, storage, and refuse disposal areas.

Objectives of Homer City Pre-Operational Monitoring

The recent construction of an advanced coal cleaning facility at the Homer City Power Complex near Homer City, Pennsylvania, provided a unique opportunity to obtain environmental data both before and after operation of the plant. Thus, in order to document the abundance or concentrations of selected key parameters, Battelle conducted a series of pre-operational, multimedia, grab-sampling campaigns in a study area that included this facility. These data were used to evaluate the air, water, and biological quality in the study area. The pre-operational environmental studies, while not sufficiently long-term to constitute a true baseline analysis, were conducted prior to operation of the cleaning plant as a reference point for future, more comprehensive, environmental testing planned during operation of the plant.

Specific Objectives of This Paper

The objective of this paper is to present some of the preoperational monitoring data from Battelle's study area near Homer City, Pennsylvania, and to compare these data with the values listed in the Multimedia Environmental Goals (MEG) documents prepared for the U.S. EPA by Research Triangle Institute (Cleland and Kingsbury, 1977a and b). The MEG values considered in this paper represent the maximum levels of significant contaminants which are not considered to be hazardous to man or the environment. The MEG methodology was developed to facilitate the evaluation and ranking of pollutants for the purpose of environmental assessment of energy-related processes.

MEG values have been estimated for 216 pollutants by extrapolating various toxicity data by means of simple models. For most of these pollutants, maximum values have been estimated for each of the three media (air, water, and land). For each of the three media, separate maximum values have been estimated which are not considered to be hazardous to (1) human health and (2) entire ecosystems.

The MEG values that are particularly appropriate for comparison with the environmental monitoring data from Battelle's study area are those designated as estimated permissible concentrations (EPC's). EPC's are the maximum concentration of a pollutant which presents no hazard to man or biota on a continuous long-term basis. These EPC values are considered acceptable in the ambient air, water, or soil, and do not apply to undiluted effluent streams. The ambient application of EPC's corresponds to the ambient type of sampling conducted by Battelle prior to operation of the Homer City Coal Cleaning Plant.

A second type of MEG values considered in this paper is one comprised of minimum acute toxicity effluent (MATE) values. MATE's are concentrations of pollutants in undiluted effluent streams which will not adversely affect those persons or ecological systems exposed for short time periods. Very little of the pre-operational monitoring conducted by Battelle near Homer City involved undiluted effluents, but in the case of a few pollutants, this value was the only MEG value determined.

Description of the Study Area

Nearly all of Battelle's environmental monitoring was conducted within a study area that can be approximately bounded by a circle 4 miles (6.4 km) in diameter. The advanced coal cleaning plant in the center of the study area is about 2 miles (3.2 km) southwest of Homer City, Pennsylvania. Only two of the aquatic biota sampling stations were slightly outside of the circular study area.

The six major habitat types within the study area are hardwood forest, coniferous forest, cropland, grassland, water bodies, and areas of industrial development. The forested areas are primarily hardwoods, dominated by oak and hickory. Isolated pockets of pine are present as plantations rather than naturally occurring species. Cropland is extensive in the study area, including contour and strip-cropped fields of corn, wheat, and hay. Grasslands include those areas that are presently grazed and those areas that were previously grazed or farmed and are now in a transition stage toward becoming a forest.

Stream water quality evaluated within the study area is affected by a number of land uses which are either included in the immediate study area or take place at locations farther upstream. The five major land uses affecting stream water are: agriculture, mining, urban, construction, and power generation. Agricultural runoff is a problem because of the hilly terrain and includes runoff from both farmland and pastures. Almost the entire study area is on top of deep mines, while much of the upstream watersheds add acid mine drainage from abandoned or active strip mines. As indicated earlier, Homer City, Pennsylvania, is immediately adjacent to the study area on the northeast, and Indiana, Pennsylvania is only 5 miles (8.0 km) north of Homer City. Both towns directly or indirectly add effluents from industrial and sewage treatment facilities to Two Lick Creek before it flows through the study area. During Battelle's sampling campaigns, both the coal cleaning plant and the refuse disposal area for that facility were under construction in the study area. Finally, the study area includes the Homer City Power Station, with its associated coal storage, water treatment, and waste disposal facilities.

The Homer City Station is one part of an integrated power complex which includes two deep coal mines; coal cleaning, storage, and transport facilities; power generation facilities; and waste disposal and treatment facilities (Figure 1). Coal used at the Homer City Station comes from the two dedicated deep mines in the power complex, as well as that hauled by truck from other mines. Solid refuse from power complex activities is deposited in three different types of disposal areas, including an ash disposal area, mine waste or "boney" piles, and the cleaning plant refuse disposal area. Liquid waste treatment facilities in the power complex include: mine and boney pile leachate water treatment facilities, an emergency holding pond constructed near the coal cleaning plant, coal storage pile runoff desilting ponds, an industrial waste treatment plant, power plant storm runoff desilting ponds, bottom ash sluice water desilting ponds, sewage treatment facilities, and ash disposal area leachate treatment ponds.

SAMPLING AND ANALYSIS TECHNIQUES

During the period from December 1976 through April 1977, a series of three pre-operational, grab-sampling campaigns were conducted by Battelle in the ambient media of the study area which included the Homer City Power Complex. These environmental monitoring studies involved sampling, laboratory analysis, and/or evaluation of the following components of the environment.

- Fugitive dust
- Stream water and sediments

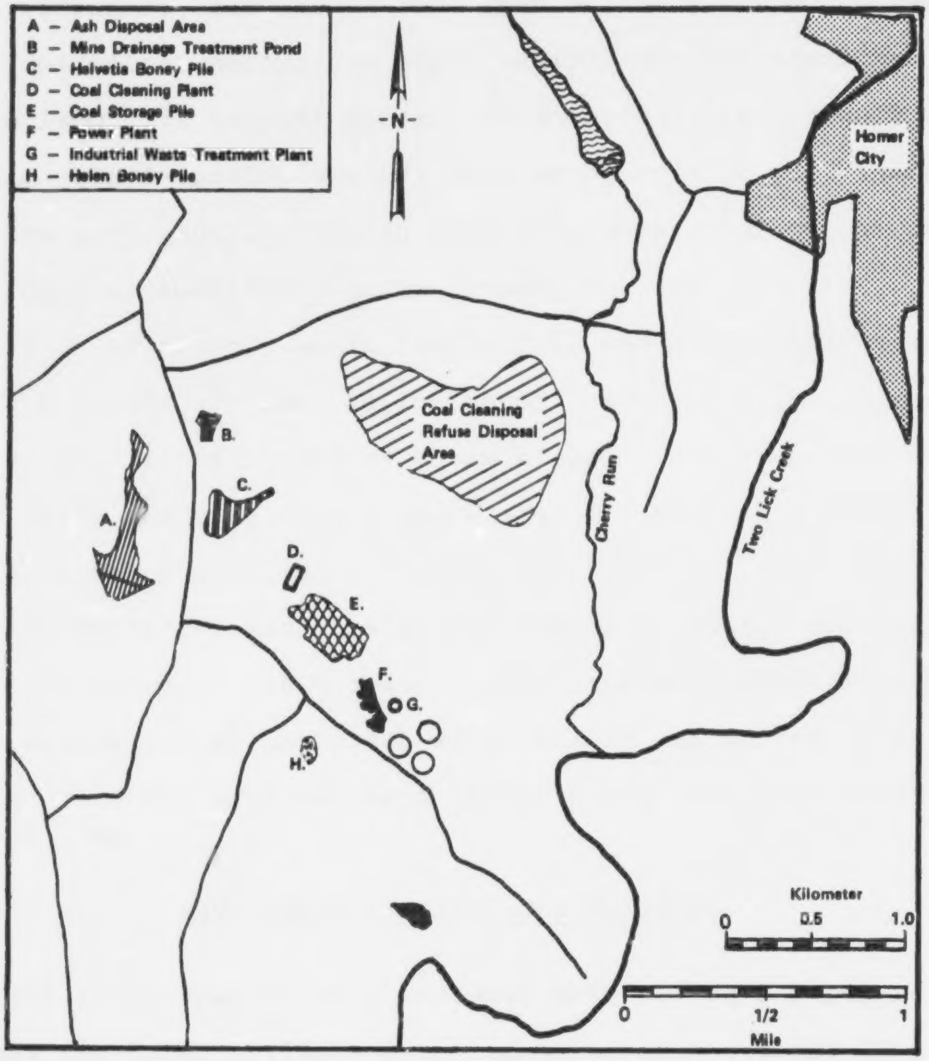

Figure 1. Map of the Homer City Power Complex

- Aquatic biota
- Terrestrial biota
- Raw coal and fly ash
- Cleaning plant refuse disposal area
- Groundwater.

Only the first three were analyzed in sufficient detail to warrant comparison with MEG values. Samples of fugitive dust, water, and stream sediments were collected during three campaigns and analyzed for physical and chemical parameters. Aquatic biota were sampled during two campaigns for determination of indicator species, standing crop, species diversity, and chemical analysis of fish.

Fugitive Dust

Fugitive dust monitoring was conducted using high-volume (hi-vol) ambient air samplers during the following three 48-hour sampling periods:

- Campaign I: 8 p.m. December 17 to 8 p.m. December 19, 1976
- Campaign II: 8 p.m. January 5 to 8 p.m. January 7, 1977
- Campaign III: 8 p.m. April 5 to 8 p.m. April 7, 1977.

The first of these three campaigns was conducted over a weekend when both coal transfer and construction activities were low.

A multiple-source fugitive-dust dispersion model was used to select and verify locations for hi-vol samplers (Figure 2). This model takes into account such factors as wind speed, emission rate, particle size, and distance from selected potential dust

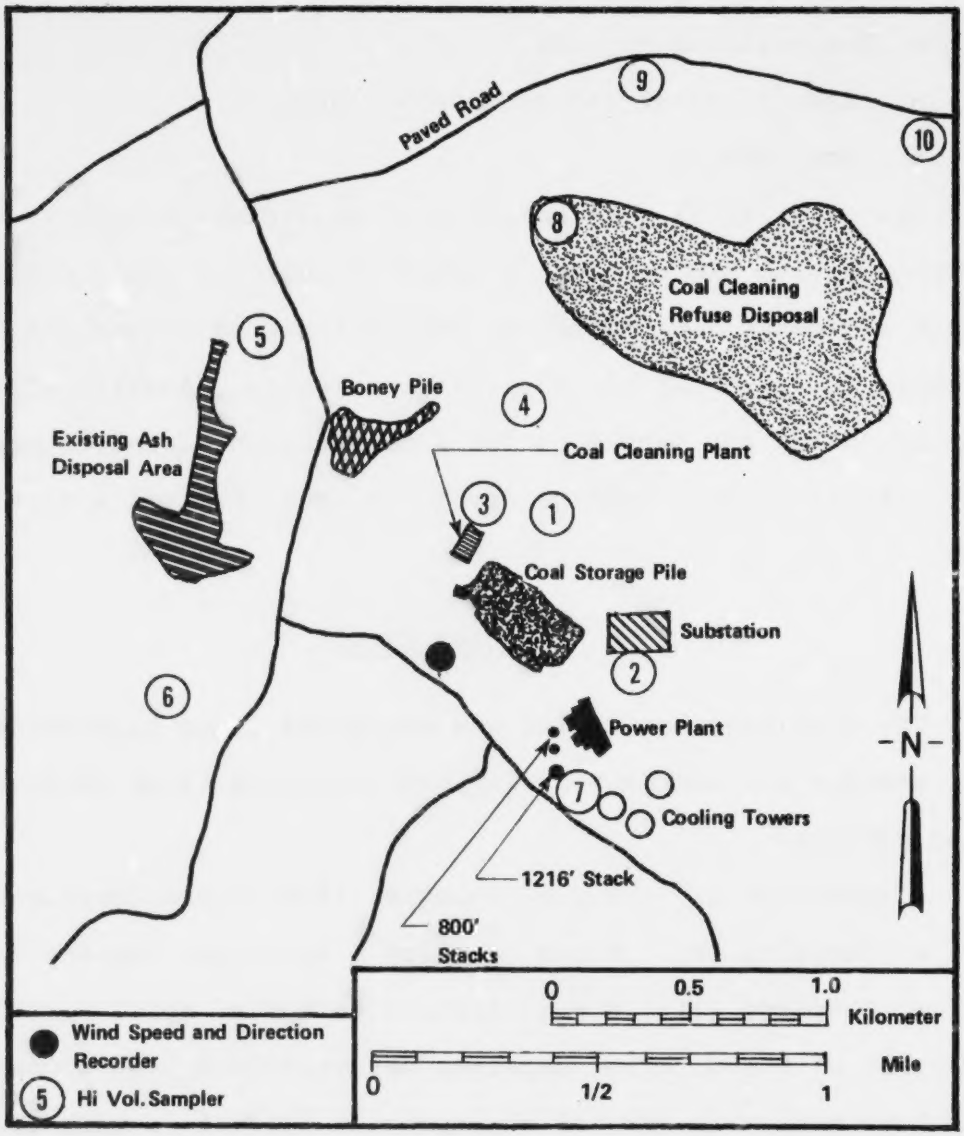

Figure 2. Location of fugitive dust sources and monitoring sites.

sources located within the Homer City Power Complex. No dust sources outside of the power complex were incorporated in the model. On the basis of the computer-generated diffusion-modeling results, ten monitoring sites were established at distances of 175 to 2200 m downwind from various local dust sources. One of the ten sites was on private property downwind of the power complex, while another was on private property upwind of the complex.

Several potential dust sources, both local and regional, were not incorporated into the diffusion model for sampling site selection. Dust generated by vehicular traffic, parking lots, construction activities, several storage silos, and especially that originating from the surface of the plant grounds were not included in the model because of their erratic and nonpoint-source nature. Data for the Homer City Power Plant stack emissions were not available in time to include them in the model. In addition, four other major power stations (Keystone, Conemaugh, Seward, and Shawville) are located in the same Chestnut Ridge sector of the Allegheny Mountains as Homer City. These utilities are fed from coal mines located either directly under or near the station sites. The model did not include fugitive emission data from any of these facilities.

Potential fugitive dust sources at the Homer City Power Complex were investigated during a pre-sampling site evaluation. Some of the dust sources included an ash disposal area, boney piles at both deep mines, a coal storage pile, road dust, three power plant stacks, and construction-generated dust. The coal cleaning plant with its thermal dryers and the cleaning plant refuse disposal area were under construction during Battelle's sampling campaigns. Since these two areas were considered to be future potential sources of fugitive dust, they were considered in the selection of sampling sites.

In order to identify the type and quantity of pollutants being emitted from fugitive dust sources, a variety of analytical techniques were employed. Particulate mass was determined by weighing the 8 x 10-inch fiberglass filters used in the hi-vol samplers before and after each of the 12- or 24-hour sampling periods. A microscopic analysis was made of particulates to provide a distinction between components such as coal dust, fly ash, pollen, or construction dust. An Andersen sampling head was used on one hi-vol sampler to obtain data on the distribution of particles in five size fractions.

Particulates on the filters from the hi-vol samplers were analyzed for up to 22 elements. The analytical technique used for most elements was atomic absorption, but neutron activation, colorimetry, a specific ion meter, a total organic carbon analyzer, an LDC mercury monitor, and potentiometric titration were also used. Since large amounts of four of these 22 elements (Na, K, Ca, and Mg) were found in the blank filters, the values for these four elements were not reported. Four of the remaining 18 elements (Sb, Ti, V, Se) were analyzed only in the second or third campaign. In general, the filter exhibiting the highest percentage of coal or ash from each site was used for analysis. Data for 15 of the elements are compared in this paper.

Stream Water and Sediments

A wide variety of water and sediment quality parameters were selected for analysis in the streams and tributaries in the study area (Figure 3). The selection of water and sediment quality parameters was based on the diversity of land use in the general area, including farming, mining, urban, construction, and power generation activities. The analytical techniques for water and sediment samples were numerous and involved the techniques suggested in the following seven references: American Society of Agronomy and ASTM (1965), Hem (1970), Stumm (1970), Stumm and Lee (1960), Stumm and Morgan (1970), U.S. Department of the Interior (1974), and U.S. Environmental Protection Agency (1969). In this paper, analytical results for 30 water quality and 9 sediment quality parameters are used for comparison with MEG values.

The sampling locations for surface water and stream sediments were selected in advance of field monitoring (Figures 4 and 5). The order of sampling was always from downstream to upstream. All sites within a given watershed were sampled on the same day or on two consecutive days.

All samples were collected in prewashed polyethylene bottles or glass jars by one of the two following methods: (1) grab sampling, and (2) use of an automatic sampler. Grab sampling consisted of submerging each container while keeping it as close to

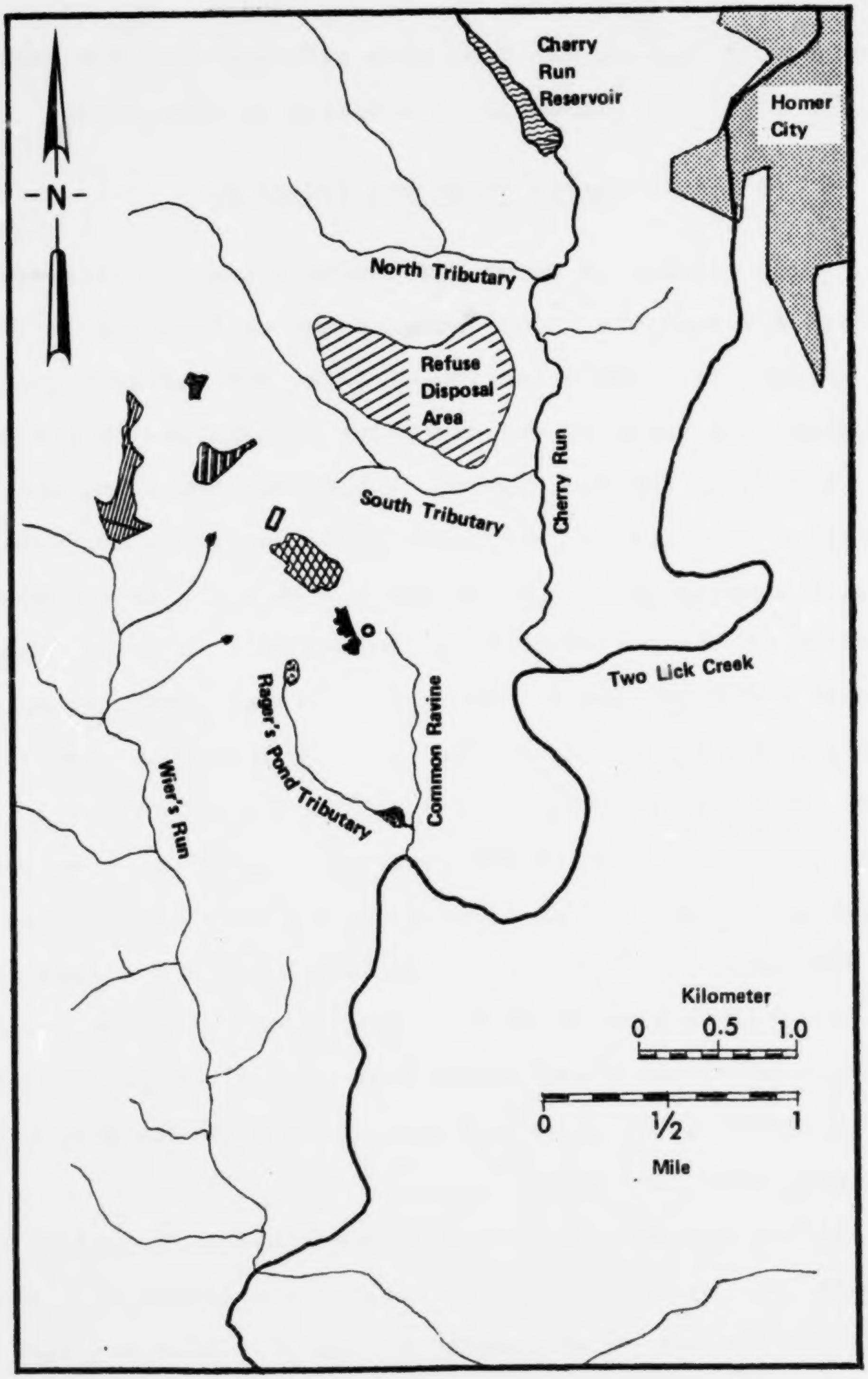

Figure 3. Streams and tributaries surveyed in the Homer City area.

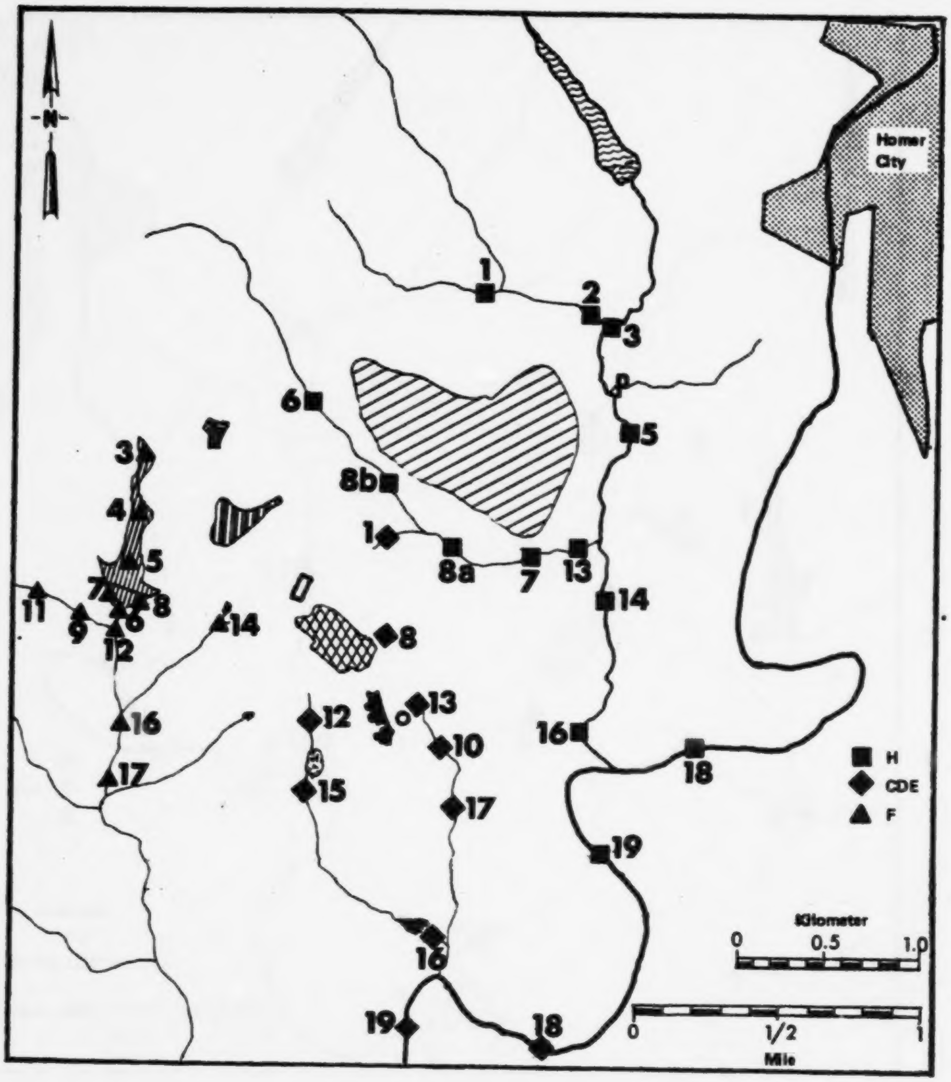

Figure 4. Surface water quality sampling locations.

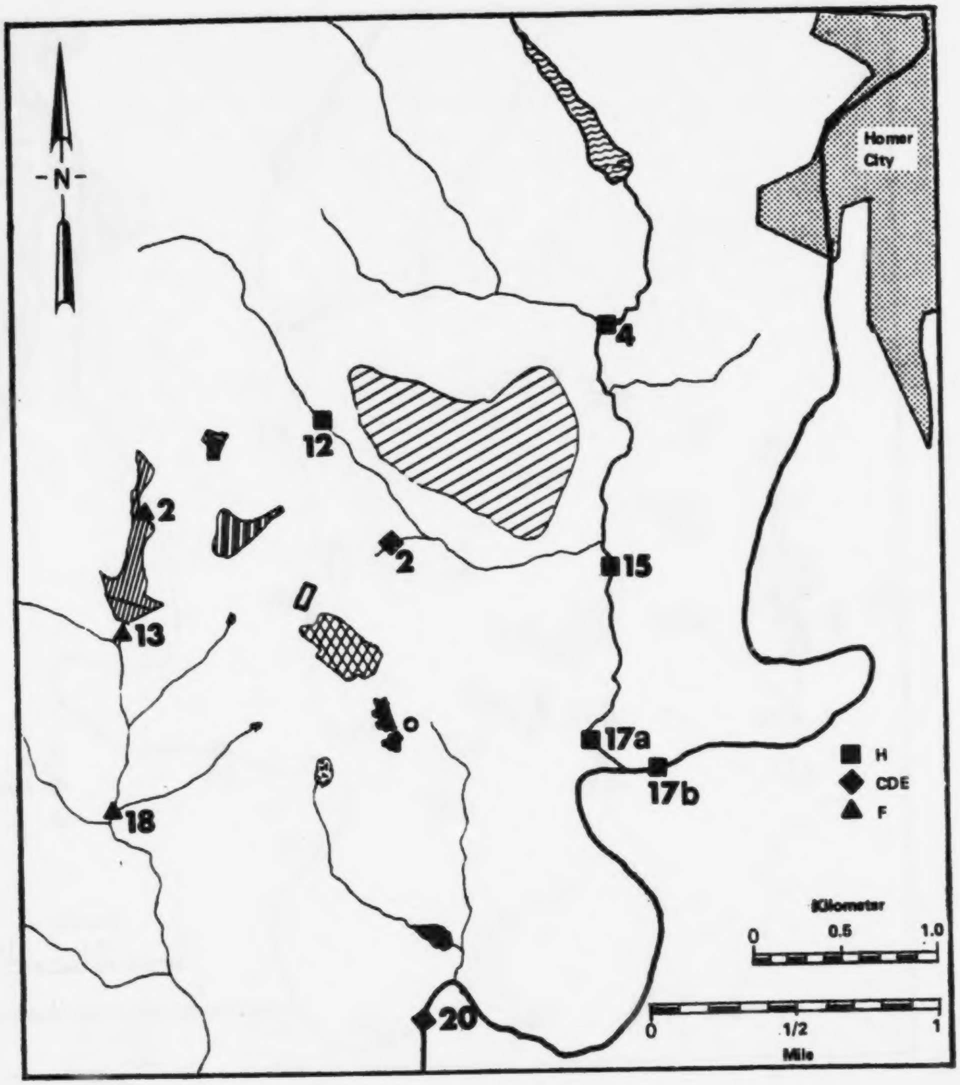

Figure 5. Stream sediment sampling locations.

the surface as possible to prevent disturbing the bottom sediment. The automatic composite sampler (Instrumentation Specialties Company, Model 1580) was used at two sites where the water quality was more variable.

Additional data were recorded at each site while collecting the sample. A Yellow Springs Instrument Company polarographic D.O. meter was used to measure the dissolved oxygen content and temperature, while a Beckman Solu-Bridge was used for specific conductance determinations. Current measurements were taken with a Price-type current meter (Pygmy meter). Flow was estimated using the velocity-area method.

Sediment samples were obtained from several streambeds. Sediment was defined as any material that would pass through a 10-mesh screen. There was difficulty in obtaining an adequate sample at some sites where the streambed was composed largely of gravel.

Aquatic Biota

Fourteen aquatic biota sampling sites were selected in seven streams in the study area, as well as in an additional control stream, Ramsey Run, which is about 6 miles (9.6 km) north-northeast of the study area and about 1 mile (1.6 km) east of Indiana, Pennsylvania (Figure 6). Sites were chosen which would provide the best data for evaluating the impact of the existing facilities in the complex on the aquatic biota of the receiving streams. Sampling was conducted both upstream and downstream from potential

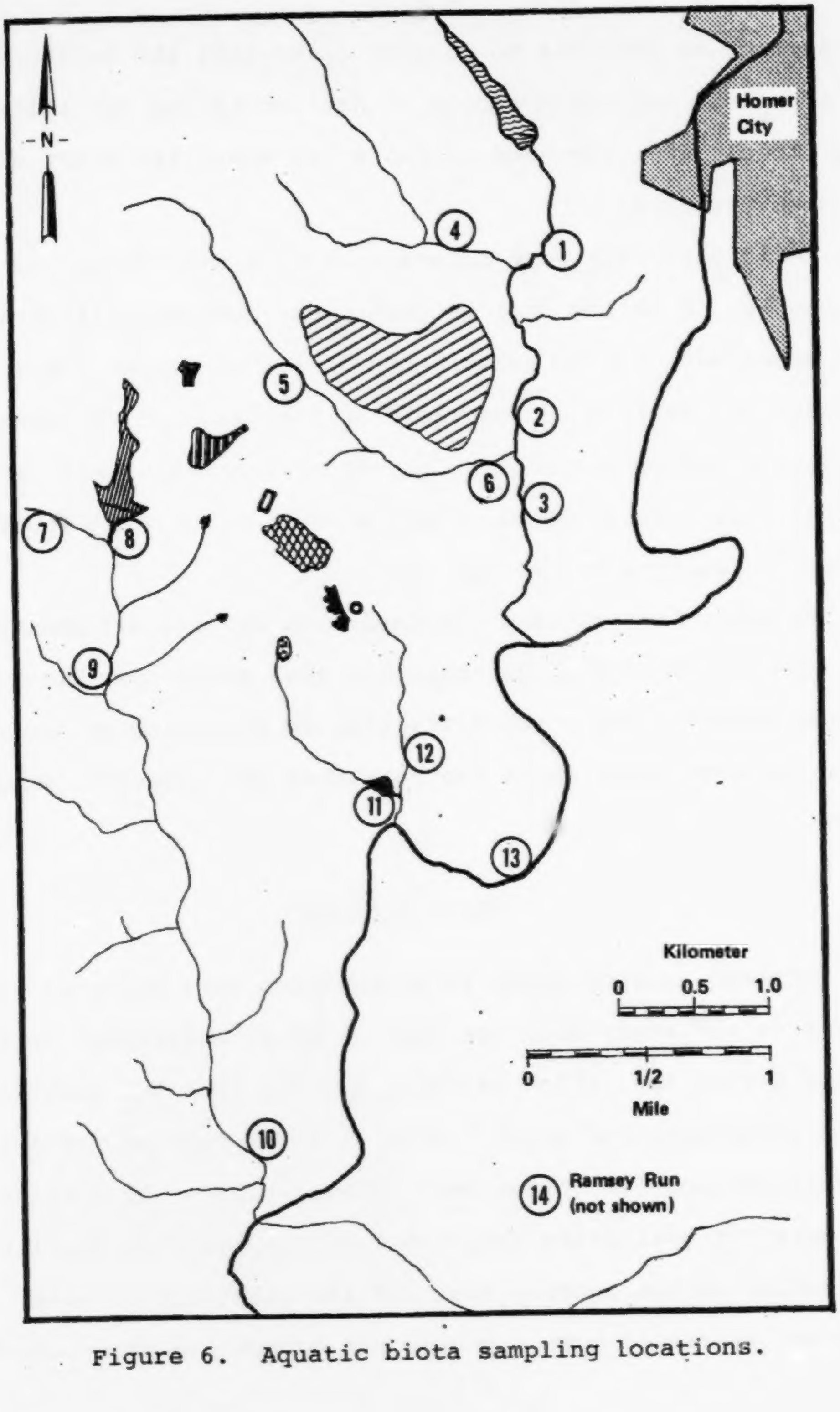

Figure 6. Aquatic biota sampling locations.

sources of pollution. Thus, the prior effect of upstream sources of pollution on aquatic biota was included in the assessment of the study area. Only a minimal sampling effort was carried out in Two Lick Creek because a survey by Environmental Sciences, Inc., (1972) reported that this stream had poor water and aquatic biota quality due primarily to acid mine drainage from abandoned strip-mines located upstream.

Three groups of aquatic organisms were selected for study: (1) periphyton (attached algae, especially diatoms), (2) benthic macroinvertebrates (bottom-dwelling invertebrates visible to the naked eye), and (3) fish. These three groups of organisms were chosen because of their relative ease of collection, usefulness as water quality indicators, and importance in aquatic food webs.

Attached algae were sampled in triplicate by scraping cobble-size rocks from the stream bottom. The preserved diatoms were prepared for viewing on a microscope slide and identified to species. Standing crop was expressed for each species in terms of number of organisms/cm^2. Finally, total periphyton standing crop and total number of species identified were calculated for each sampling site.

Bottom-dwelling macroinvertebrates were collected from riffle areas using a Surbur sampler. Five replicate samples were taken at all stations and were preserved with formalin and returned to Battelle for sorting, identification, and enumeration. All organisms were identified to the lowest practical taxon, and the resulting data were used to calculate species diversities according to the Shannon-Weaver formula (Shannon and Weaver, 1963).

Fish were collected by using a 4 x 6-ft, 1/4-in-mesh seine and/or a backpack shocker. Both devices were used during the spring survey, but only the seine was used during the winter survey. Fishing was conducted with approximately equal effort (1/2 hour) at each station. Fish were identified, recorded, and released. Specimens not positively identified in the field were placed in sample bottles, preserved, and returned to the laboratory for identification.

Biological quality was determined for each of eight portions of streams or tributaries surveyed in the study area. Quality of the biota in the control stream (Ramsey Run) was evaluated as good and provided a basis for comparing the other streams. The subjective evaluation of aquatic biota quality in each stream was determined by initially evaluating each of the three groups of organisms surveyed. The evaluations were based on the presence of indicator species, standing crop of diatoms, species diversity of bottom-dwelling macroinvertebrates, and number of individuals per fish species. Finally, overall biological quality ratings of good, fair, or poor were based on the individual ratings for the three aquatic biota groups.

COMPARISON OF ANALYTICAL DATA WITH MEG VALUES

Analytical data for fugitive dust, fly ash, raw coal, surface water, and stream sediments sampled in the study area have been converted to the units used in the multimedia environmental goals (MEG) study (Cleland and Kingsbury, 1977a and b). These data are compared with the estimated permissible concentrations (EPC's) and/or the minimum acute toxicity effluent (MATE) values defined in the Introduction to this paper. In addition, the observed and recommended values for stream water and sediments are compared with the biological quality evaluations made at sampling locations in the same portion of a given stream.

Fugitive Dust Analysis

Average concentrations of 15 elements analyzed in the fugitive dust from the study area are compared with the EPC's for air in Table 1. Since most of the fugitive dust appeared to emanate from the coal storage pile and decline in concentration within 200 to 300 m downwind (Figure 7), the data have been averaged for the sampling sites located between 150 to 175 m and 400 to 1,800 m downwind from the coal pile. The fugitive dust concentrations for the upwind "control" sampling location are also provided. These field data are followed by the appropriate maximum EPC's for air which are recommended for each element to prevent negative effects to humans or the surrounding environment during continuous long-term (chronic) exposure. A difficulty in making comparisons between observed and recommended levels of the 15 elements shown in Table 1 is that three EPC's for human health and 10 EPC's for the environment are not available.

Average concentrations for three of the elements (As, Cr, and Pb) analyzed in fugitive dust exceeded the EPC's for human health.

Table 1. Fugitive dust comparisons ($\mu g/m^3$): EPC values for air versus Homer City data

	Trace Element Concentrations, $\mu g/m^3$														
	As	Cd	Cr	Cu	Fe	Pb	Mn	Hg	Ni	Ti	Zn	Cl	F	V	Se
Distance from Coal Pile	Average Concentration in Fugitive Dust During 3 Campaigns at Homer City (24-hr Sampling Periods)(a)														
Downwind 150-175 m(b)	0.014	0.008	.026	0.292	3.45	0.586	0.076	0.00056	0.015	0.44	0.35(i)	1.97(i)	5.47	ND(j)	0.0049
Downwind 400-1,800 m(c)	0.010	0.014	.015	0.119	1.87	0.334	0.093	0.00009	0.013(i)	0.32(i)	0.22	0.82	2.03	ND	0.0026(i)
Upwind Control(d)	0.009	0.005	.014	0.223	1.65	0.258	0.041	0.00003	0.009	0.17(i)	0.13	1.05	1.40	0.02(i)	0.0030(i)
EPC Category	Estimated Permissible Concentrations (EPC's)(e), $\mu g/m^3$														
Health	0.005	0.12(f)	0.002(f)	0.5	—(h)	0.36	12	16(f)	0.04(f)	14	9.5	—	—	1.2	0.5
Ecology	—	0.04(g)	—	—	—	1(g)	—	0.01(g)	—	—	—	—	—	0.1	0.03(g)

(a) All data were collected between December 1976 and April 1977.
(b) Average for sampling sites 1 and 3; downwind of coal pile.
(c) Average for sampling sites 4, 8, and 9; downwind of coal pile.
(d) Sampling site 6; upwind of coal pile about 1600 m and off of the power station property.
(e) From Cleland and Kingsbury (1977).
(f) Based on a Toxic Limit Value (TLV) which recognizes the element's carcinogenic potential
(g) Based on teratogenic potential.
(h) Not available.
(i) Concentrations were not available for some sampling sites during all three campaigns.
(j) ND = not detectable.

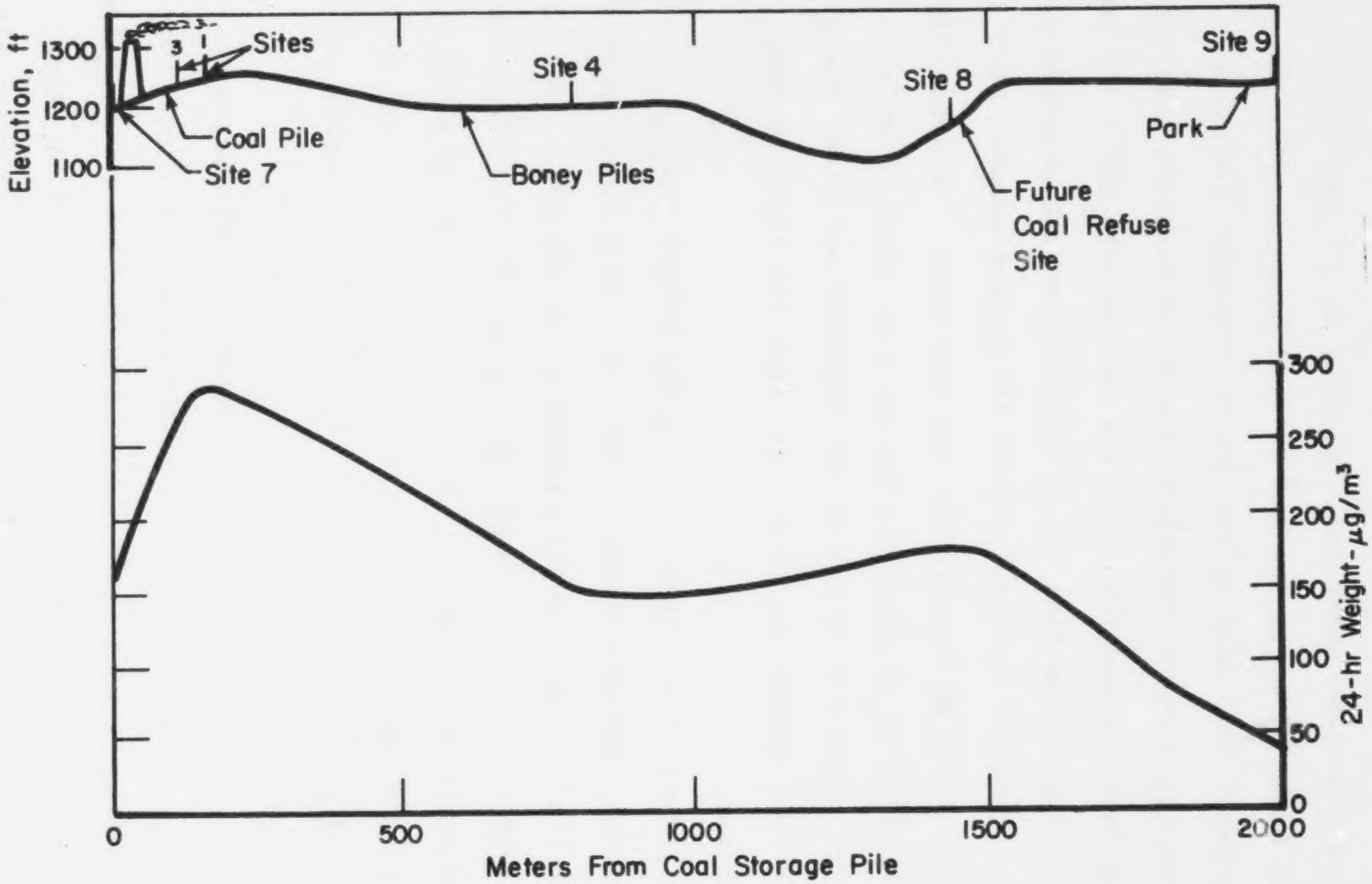

Figure 7. Fugitive dust concentrations compared to a transect of the area's topographical relief.

These values have been underlined in Table 1. It is noteworthy that two of these elements (As and Cr) had concentrations above the health-based EPC, even at the upwind "control" location.

Maximum and minimum concentrations of 15 elements analyzed in fugitive dust are compared with the appropriate EPC's for soil in Table 2. Again, the data are grouped to include sampling sites located less than 200 m (i.e., 150 to 175 m) and greater than 200 m (i.e., 400 to 1,800 m) downwind of the coal pile. Concentrations of the same elements in the raw coal are also shown. EPC's for protection of human health and the environment are given for 12 elements; no EPC values for iron, chlorine, and fluorine have been determined.

The majority of the elements analyzed showed maximum, and frequently minimum, concentrations in the fugitive dust which were far greater than the EPC levels suggested for the soil. Ten elements exceeded the EPC's for human health and 11 elements exceeded the EPC's for the environment. Both the maximum and minimum concentrations of 8 elements (As, Cd, Cr, Cu, Pb, Mn, Ni, and Se) in the fugitive dust exceeded the EPC's for both human health and the environment.

Obviously, the detected concentrations of toxic trace elements in fugitive coal dust that has settled to the ground surface do not indicate that these same concentrations occur in the soil. However, studies involving soil contamination by other types of particulate deposition have shown that toxic trace elements in these particulates can cause ecosystem disruption

Table 2. Fugitive dust comparisons (μg/g): EPC values for soil[(a)] versus Homer City data

	Trace Element Concentration, μg/g														
	As	Cd	Cr	Cu	Fe	Pb	Mn	Hg	Ni	Ti	Zn	Cl	F	V	Se
	Concentrations in Particulate at Sampling Sites within 200 m of Homer City Coal Pile (Sites 1 and 3)[(a)]														
Maximum	154	264	471	3,678	28,736	17,241	632	3	264	8,676	3,563	39,081	55,000	ND	33
Minimum	11	18	18	336	6,223	501	65	0.2	23	626	ND[(f)]	4,043	ND	ND	4
	Concentrations in Particulate at Sampling Sites Between 200 and 2 000 m of Homer City Coal Pile (Sites, 4, 8, and 9)[(a)]														
Maximum	238	619	667	6,061	57,576	12,857	5,603	2	545	3,007	5,152	27,278	45,600	ND	122
Minimum	34	ND	46	220	11,477	566	6	ND	ND	1,356	943	5,806	1,818	ND	1
	Estimated Permissible Concentrations (EPC's) for Soil[(b)]														
Health	10	0.06[(c)]	0.01[(c)]	200	--[(e)]	70[(c)]	10	50[(c)]	0.1[(c)]	17	1,000	--[(e)]	--[(e)]	1.4	2
Ecology	2	0.01[(d)]	10	20	--[(e)]	1[(d)]	4	1[(d)]	0.4	800	4	--[(e)]	--[(e)]	15	0.1[(d)]
	Raw Coal Concentrations Determined by Individual Analysis of Three Homer City Coal Sources[(g)]														
Maximum	48	0.26	35	31	48,750	17.3	74	1.1	16.8	1,329	66	0.26	108	65	ND
Minimum	22	<0.1	30	20	18,000	12	35	0.34	12.8	1,125	46	0.23	91	55	ND

(a) Data from three sampling campaigns conducted by Battelle in the study area.
(b) From Cleland and Kingsbury (1977); all values were multiplied by 100 based on personal communication with Kingsbury (August, 1978).
(c) Based on carcinogenic potential.
(d) Based on teratogenic potential.
(e) Value not available.
(f) ND = not detectable.
(g) Coal sources include: Helen Mining Company and Helvetia Coal Company (from Upper Freeport Seam); and Trucked-in Coal (from Lower Kittanning Seam).

resulting in the loss of essential nutrients and can also result in increased concentrations of these toxic elements in both plants and animals. These types of effects have been demonstrated for lead smelter emissions (Jackson and Watson, 1977; Kerin, 1975) and for fly ash emissions from coal-fired power plants (Furr et al., 1977). Dvorak et al. (1978) have speculated that long-term exposure to uncombusted coal dust may cause changes in vegetation community structure similar to those caused by particulates from coal combustion.

Mechanisms for the movement of toxic trace elements from particulate emissions deposited on the ground to the root zone of the soil are complex (Vaughan et al., 1975; Dvorak et al., 1978). A partial list of the factors that influence leaching of trace elements from deposited particulates into the soil solution include: (1) the size and type of particulates, (2) the amount and acidity of precipitation, (3) the concentrations and physicochemical properties of the trace elements, (4) the texture, organic content, pH, and other characteristics of the soil, (5) the solubility of elements into the soil solution, and (6) the temperature of the air and soil.

The fugitive dust quantity and composition found during monitoring has probably been accumulating on the ground in a reasonably similar fashion since the power plant (including the coal storage pile) began operation in 1969. Thus, mobile elements in the settled dust may have leached into the soil. The quantity of toxic trace elements available to vegetation, however, needs to be determined by chemical analysis of the soil. In spite of any leaching of trace elements which may have increased soil concentrations, vegetation growing within a broad band around the coal pile has not yet experienced any apparent adverse effects. An analysis of soil biota and plant diversity, however, was not conducted.

Stream Water, Sediments, and Biota Analysis

Stream Water Concentrations Versus MEG Values

Maximum and minimum concentrations of 15 elements that were analyzed in surface water are compared with the appropriate MATE and EPC values for the environment in Table 3. These data were organized to correspond to the biological sampling locations for additional comparisons. Although data were obtained in the study area near Homer City for 30 different parameters used to define water quality in stream water, MEG values are only available for the parameters listed in Table 3.

EPC and MATE values suggested for the environment were exceeded by many of the maximum and minimum values determined for the 15 water quality parameters listed in Table 3. Maximum values for nine parameters measured in surface water throughout the study area exceeded the corresponding MATE values, and maximum values for 11 parameters exceeded the corresponding EPC values. Maximum and minimum values of measured parameters exceeded EPC's in the following 10 cases: beryllium, lead, ammonia, nitrogen, arsenic, manganese, nickel, copper, zinc, and cadmium.

Table 3. Surface water quality comparisons (μg/l): MEG values versus Homer City data[(a)]

MEG Category and Substance		Minimum Acute Toxicity Effluent (MATE) for Ecology	Estimated Permissible Concentration (EPC) for Ecology	Streams in the Vicinity of Homer City Station: Cherry Run: Main Stem		North Tributary to Cherry Run		South Tributary to Cherry Run: Upstream		South Tributary to Cherry Run: Downstream		Wier's Run Below Ash Disposal Area		Tributary to Wier's Run		Rager's Pond Tributary		Common Ravine		Two Lick Creek		Reference Stream Dec-Apr Average[(e)]
				Water Quality Evaluation[(b)]																		
				Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	
18	Phenolics	500	100[(d)]	—[(c)]	—	—	—	—	—	—	—	10	ND	7	6	340	9	360	30	8	ND	—
32	Beryllium	55	11[(d)]	ND[(f)]	ND	ND	ND	ND	ND	ND	ND	ND	ND	—	—	20	20	ND	ND	ND	ND	—
34	Calcium	16,000	—	23,600	16,500	20,300	17,400	38,900	19,200	37,200	7,200	208,500	84,000	—	—	209,000	113,000	485,000	102,500	43,900	21,000	3,500
46	Lead	50	10[(b)]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30	20	ND	ND	1
47	Ammonia Nitrogen	50	10[(d)]	80	<50	60	<50	50	<50	<50	<50	630	180	—	—	14,400	360	4,200	1,600	1,280	190	—
49	Arsenic	50	10[(d)]	ND	ND	ND	ND	ND	ND	ND	ND	8	ND	ND	ND	20	ND	60	20	ND	ND	<1
65	Vanadium	150	15[(d)]	ND	ND	ND	ND	300	ND	ND	ND	ND	ND	—	—	ND	ND	ND	ND	ND	ND	—
69	Chromium	250	50[(d)]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	40	20	ND	ND	<10
68	Chromium+6	250	50[(d)]	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	ND	ND	—
71	Manganese	100	20[(d)]	460	20	280	20	210	130	1,400	<20	6,100	1,400	—	—	45,200	2,210	1,760	680	1,300	550	20
76	Nickel	10	2[(d)]	ND	ND	ND	ND	ND	ND	ND	ND	100	70	ND	ND	640	80	140	60	ND	ND	—
78	Copper	50	10[(d)]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	60	ND	50	30	ND	ND	0
81	Zinc	100	20[(d)]	20	ND	20	20	50	50	50	30	120	90	40	ND	1,730	100	290	230	110	80	0
82	Cadmium	1	0.4[(d)]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	ND	1	1	ND	ND	0
83	Mercury	250	50[(d)]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<0.5
				Biological Quality Evaluation[(g)]																		
Attached Algae				F		F		F		P		F		G		P		P		P		
Bottom-Dwelling Invertebrates				P		G		G		P		P		G		P		P		P		
Fish				F		G		G		F		P		G		P		P		P		
Overall Rating				F		G		G		P		P		G		P		P		P		

(a) All values are given in μg/ℓ; EPC and MATE values are from Cleland and Kingsbury (1977).
(b) Data from three sampling campaigns conducted by Battelle in the study area
(c) Data not available.
(d) Based on most stringent existing or proposed Federal standard for water quality.
(e) Chemical analysis during water year 1973 of Young Women's Creek near Renovo, Pa.
(f) ND = not detectable.
(g) The aquatic biota evaluations are based on standing crop, species diversity, and presence of indicator species or families; G = Good; F = Fair; and P = Poor Aquatic Biota Quality. Data are from two sampling campaigns conducted by Battelle in the study area

Streams considered to have good biological quality also had levels of pollutants which exceeded EPC or MATE values for the environment. Maximum and minimum levels of manganese and zinc in streams with good aquatic biota quality exceeded the EPC values for the environment. Maximum levels, alone, of two additional parameters (ammonia and vanadium) in streams with good aquatic biota quality also exceeded the EPC values for the environment. Similarly, maximum and minimum levels of calcium and manganese in streams with a good biological quality rating exceeded the MATE values for the environment.

Stream Water Concentrations Versus Recommended Values

MEG values have not yet been determined for 14 of the 30 water quality parameters measured in Battelle's study area. Therefore, comparisons have been made between these 14 parameters and 8 values recommended by the EPA (1976) or suggested by McKee and Wolfe (1963) (Table 4). A biological quality evaluation of the same stream stretches that were analyzed for water quality is presented for comparison with the chemical data.

All eight of the water quality criteria concentrations recommended by EPA (1976) or McKee and Wolf (1963) were exceeded by one or more concentrations of the same parameters measured in samples from streams in the study area (Table 4). The maximum and minimum values for alkalinity, sulfate, and total solids observed in one of the streams with a good biological quality rating were greater than the recommended criteria concentrations.

Table 4. Surface water quality comparisons (μg/l): Recommended criteria versus Homer City Data[(a)]

Water Quality Parameter	Recommended Criterion: Freshwater Aquatic Life		Streams in the Vicinity of Homer City Station: Cherry Run: Main Stem		North Tributary To Cherry Run		South Tributary To Cherry Run: Upstream		South Tributary To Cherry Run: Downstream		Wier's Run Below Ash Disposal Area		Tributary To Wier's Run		Rager's Pond Tributary		Conemaugh Barrier		Two Lick Creek		Reference Stream Dec-Apr Average[(d)]
	EPA[(b)]	McKee & Wolf[(c)]	Water Quality Evaluation: Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	
			Solubility Controls[(f)]																		
Acidity, as $CaCO_3$	—[(e)]	—	7,800	1,400	7,200	1,400	3,800	1,400	4,300	1,400	45,700	3,100	—		1,999,000	28,300	183,000	0	79,000	31,400	—
Alkalinity, as $CaCO_3$	≥20,000	—	44,200	13,200	44,200	21,100	19,600	12,600	15,700	7,100	60,100	11,000	—		2,400	0	615,000	0	4,300	0	3,800
pH	9.0-6.5	9.0-6.3	7.2	6.1	7.6	6.7	7.9	6.6	7.5	6.4	7.6	4.9	—		4.9	4.3	11.4	4.8	3.3	3.2	6.9-6.2
Total Fe	1,000	300	1,990	140	1,710	140	530	80	660	200	15,000	1,820	—		472,500	8,000	21,400	7,930	15,000	3,670	30,000
Dissolved Fe	—	—	760	<20	10	<20	90	<20	60	<20	13,000	20	—		453,000	7,900	8,200	20	12,400	3,930	—
Fe^{2+}	—	—	760	<100	420	<100	190	<100	170	<100	2,140	<100	—		467,000	<100	370	<100	6,030	<100	—
Sulfate (SO_4)	—	11,000	83,600	27,300	37,300	27,300	267,000	115,000	204,000	20,600	1,360,000	460,000	—		2,940,000	424,000	1,100,000	290,000	230,000	90,000	7,500
			Nutrients and Solids[(f)]																		
Total Phosphorus	100	—	40	<10	100	10	30	10	50	10	10	<10	—		<10	<10	160	<10	170	<10	10
Suspended Solids	—	30,000	14,000	2,000	10,000	1,200	10,800	1,200	29,800	6,800	35,300	11,200	—		156,000	23,600	948,000	61,250	36,500	5,600	5,000
Volatile Solids	—	—	34,000	2,000	48,000	7,000	50,000	30,000	45,000	5,000	115,000	60,000	—		738,500	830	1,046,000	2,380	76,000	24,000	—
Nitrate - N	90,000	—	2,000	760	1,420	360	1,000	500	1,070	<100	1,260	520	—		4,400	2,060	3,750	400	1,800	220	N.D.[(i)]
Total Kjeldahl - N	—	—	360	140	340	<50	270	120	160	<50	950	270	—		17,800	500	4,550	2,200	1,250	350	—
Total Organic Carbon	—	—	4,000	1,700	2,000	1,200	3,500	1,500	4,000	1,200	7,000	<1,000	—		24,800	3,000	57,500	7,250	6,300	1,800	N.D.
Total Solids	—	102,000[(g)]	103,000	124,000	159,000	124,000	442,000	180,000	380,000	82,000	2,119,000	818,000	—		4,978,500	743,000	2,260,300	579,500	438,000	305,000	
Dissolved Solids	—	—	No Data From Homer City																		26,000
			Biological Quality Evaluation[(f,h)]																		
Attached Algae			F		P		P		P		P		G		P		P		P		
Bottom-Dwelling Invertebrates			F		G		G		P		P		G		P		P		P		
Fish			F		G		G		P		P		G		P		P		P		
Overall Rating			F		G		G		P		P		G		P		P		P		

(a) All values are given in μg/l except pH units.

(b) "Quality Criteria for Water" (EPA, 1976).

(c) "Water Quality Criteria" (McKee and Wolf, 1963).

(d) Chemical analysis during water year 1973 of Young Woman's Creek near Renovo, Pa.

(e) Not available.

(f) Data from three sampling campaigns conducted by Battelle in the study area

(g) Estimated by summing the values recommended for suspended and dissolved solids.

(h) The aquatic biota evaluations are based on standing crop, species diversity, and presence of indicator species or families;
G = Good; F = Fair; and P = Poor Aquatic Biota Quality. Data are from two sampling campaigns conducted by Battelle in the study area.

(i) ND = not detectable.

A comparison of the data for each of the 30 surface water quality parameters with the biological quality evaluation for the same stream segment suggests that values for four parameters agree closely with the biological quality rating (Tables 3 and 4). The maximum and minimum values for these four parameters (pH, suspended solids, dissolved iron, and total organic carbon) have been compared with recommended or suggested water quality criteria in Table 5. It can be seen that streams with good biological quality did not have any levels of these four parameters which were above the recommended criteria. Maximum, and frequently minimum, values of these four parameters, however, exceeded the recommended criteria in streams with poor biological quality. The significance of these four "master" parameters to aquatic biota is probably great because they affect the presence of toxicity of other potential water pollutants.

Several studies have described the effects of water pollutants in acid mine drainage on aquatic biota. These studies found that the master chemical factors involved one or more of the parameters listed in Table 5. Weed and Rutschky (1972), for example, found that pH, alkalinity, and ionic concentrations of iron and sulfate were primarily responsible for altering the community structure and diversity of benthic macroinvertebrates. Similarly, Warner (1971) found that pH measurements in streams seemed to provide the most reliable, as well as unique, index of the effects of acid mine drainage on aquatic life. A report by the Federal Water Pollution Control Administration (1969)

Table 5. Water quality parameters in close agreement with biota quality rating

Water Quality Parameter	Sampling Sites (units or concentrations>specified value(a))							
	1	2	3	4	5	6	7	8
pH (6.5-9.0)(b)	1	0	0	1	1	2	2	2
Suspended Solids (20,000 µg/l)(c)	0	0	0	1	1	2	2	1
Dissolved Fe (1,000 µg/l)(c)	0	0	0	0	1	2	1	2
Total Organic Carbon (4,000 µg/l)(c)	1	0	0	1	1	1	2	1
Grand Totals	2	0	0	3	4	7	7	6
Biota Quality Rating(d)	F	G	G	P	P	P	P	P

(a) Maximum and minimum units or concentrations<specified value = 0; maximum units or concentrations>specified value = 1; maximum and minimum units or concentrations>specified value = 2.

(b) Criteria recommended by EPA (1976).

(c) Criteria suggested on the basis of the chemical and biological data presented in this paper.

(d) G = good; F = fair; P = poor quality.

concluded that acid mine drainage damages aquatic biota primarily because of the high concentrations of mineral acids, the ions of iron, sulfate, and the deposition of a smothering blanket of precipitated iron salts on the stream bed.

Sediment Concentrations Versus MEG Values

EPC values for nine trace elements (Pb, As, Cr, Mn, Ni, Cu, Zn, Cd, and Hg) which were measured in stream sediments were exceeded by both the maximum and minimum stream concentrations for eight of these elements (Table 6). Comparisons of concentrations

Table 6. Sediment quality comparisons (μg/g): MEG values for soil versus Homer City data[a]

MEG Category and Substance		MATE[b] for Ecology	EPC[b] for Ecology	Streams in the Vicinity of Homer City Station — Concentrations in Stream Sediments[c]: Cherry Run: Main Stem		Upstream On South Tributary To Cherry Run		Wier's Run Below Ash Disposal Area		Two Lick Creek		Ash Analysis[e]		Analysis of Three Raw Coals[f]	
				Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
46	Lead	10	3[d]	50	19	63	36	29	2	85	48	14	12	17.8	12.3
49	Arsenic	10	2	15	4.8	9.6	6.6	19	7.6	21.5	10	5.4	3.8	49	23
68	Chromium	50	10	346	84	225	157	197	102	152.5	90	144	112	36	31
71	Manganese	20	4	2,830	248	1,430	612	1,000	349	251.5	210	—(h)		76	36
76	Nickel	2	0.4	207	71	130	115	117	71	79	33	75	71	17.5	13.2
78	Copper	10	20	440	23	310	120	270	25	230	94	126	90	32	21
81	Zinc	20	4	387	75	677	244	210	65	207	108	73	40	69	47
82	Cadmium	0.2	0.01[d]	1.0	0.5	1.0	0.5	0.4	0.2	0.55	0.55	0.6	0.6	0.27	0.1
83	Mercury	50	3[d]	0.25	0.010	0.016	0.016	0.15	0.024	0.53	0.42	0.14	<0.005	1.1	0.35

Biological Quality Evaluation[g]

	Cherry Run: Main Stem	Upstream On South Tributary To Cherry Run	Wier's Run Below Ash Disposal Area	Two Lick Creek
Attached Algae	F	F	F	P
Bottom-Dwelling Invertebrates	P	G	P	P
Fish	F	G	P	P
Overall	F	G	P	P

(a) MEG = Multimedia Environmental Goals from Cleland and Kingsbury (1977); all values were multiplied by 100 based on personal communication with Kingsbury (August, 1978); all values in μg/g dry weight.
(b) MATE = Minimum Acute Toxicity Effluent; EPC = Estimated Permissible Concentrations.
(c) Based on three sampling campaigns conducted by Battelle in the study area.
(d) Based on potential teratogenic effects.
(e) Sampled in ash disposal area.
(f) Raw coals sampled at Homer City include those from: Helen Mining Co. and Helvetia Coal Co. (from Upper Freeport Seam) and Trucked-in Coal (from Lower Kittanning Seam).
(g) The aquatic biota evaluations are based on standing crop, species diversity, and presence of indicator species or families; G = Good; F = Fair; and P = Poor Aquatic Biota Quality.
(h) No data available.

for the same nine elements in fly ash from the ash disposal area revealed that maximum and minimum ash concentrations of six elements exceeded their associated MATE and EPC values. Maximum and minimum concentrations of all of these elements, except chromium, mercury, and cadmium, were higher in separate grab sample analyses of the three raw coals used in the Homer City Power Complex than they were in the associated MATE or EPC values. Therefore, coal and fly ash from a variety of sources may be contributing to the trace element content in the sediments of the study area streams.

In spite of the toxic trace elements in its sediments, one stream in the study area still had a good biological rating (Table 6). The upstream portion of the south tributary to Cherry Run had good biological quality. This stream, however, had maximum and minimum concentrations of seven elements (Pb, Cr, Mn, Ni, Cu, Zn, and Cd) that exceeded the associated MATE and EPC values.

Conclusions and Recommendations

Pollutant Toxicity Considerations

Several factors confounding pollutant toxicity evaluations need to be considered when comparisons are made between EPC values and field data on pollutant concentrations and biological quality. First, the EPC values have not incorporated interactive effects of pollutant combinations, such as synergism or antagonism. (Antagonistic effects between pollutants measured in stream water and sediments may explain how some EPC's for ecology were exceeded in streams that had a good biological quality rating.)

Second, EPC's and field chemical data frequently involve only total elemental concentrations. Biota in the ambient environment, however, may be adversely affected only by specific compounds or ions of an element that are relatively stable in the ambient media and not by other compounds that are included in the total elemental concentration. To date, EPC values for inorganics have been determined primarily for groups of compounds which have a common parent element; comparatively few of the individual, highly toxic compounds within these groups that are also relatively stable in the environment have been evaluated for an EPC. Third, some of the water quality parameters which are extremely important in making an environmental assessment of coal-related effluents on aquatic biota do not presently have EPC's. These master parameters, including suspended solids, pH, alkalinity, etc., are planned for future EPC evaluation.

Fugitive Dust

Elemental concentrations in fugitive dust which were measured in the study area exceeded both EPC and MATE values for air and soil quality. For example, three out of 15 elements analyzed in fugitive dust had concentrations above the health-based EPC's for air quality. Comparisons with ecology-based EPC's for air quality, however, were very difficult because of the absence of ten EPC values.

Although no soil concentrations were determined, comparisons of elemental concentrations in fugitive dust were made with ecology-based EPC's for soil because of the potential problem of toxic elements leaching into the soil from fugitive dust laying on the ground. Eleven of the 15 elements studied had concentrations in the fugitive dust which were above the ecology-based EPC's for soil. Thus, additional research needs to be conducted to determine if leaching is a problem. The existence of this type of problem, however, seems to be inconsistent with the condition of the vegetation in the area. In spite of the dust (particularly coal dust) present on the ground for some distance around the coal pile, the vegetation has not yet begun to show any obvious adverse effects.

Stream Water, Sediments, and Biota

Of the 30 water quality parameters measured in streams, only 15 parameters have associated MEG values. Thus, some of the surface water quality data were compared with the MEG's and some were compared with other available criteria. The maximum and minimum of 10 parameters exceeded the corresponding EPC's for the environment. In fact, maximum, and some minimum levels, of four pollutants (ammonia, vanadium, manganese, and zinc) exceeded the appropriate EPC values, even in streams considered to have good biological quality. This apparent discrepancy needs to be further evaluated both in terms of the validity of the proposed EPC values used, and in terms of the interactions and uniqueness of the chemical and biological conditions encountered in the study area streams.

Fifteen water quality parameters evaluated in Battelle's study do not have corresponding MEG values; these parameters were compared with criteria from the EPA (1976) and McKee and Wolf (1963). Values for four of these parameters (pH, suspended solids, dissolved iron, and total organic carbon) were in close agreement with the biota quality evaluation.

Elemental concentrations in stream sediments were considerably higher than the corresponding MEG values. Maximum and minimum concentrations of eight elements in sediments exceeded the associated EPC's and MATE's for ecology. This situation occurred for seven elements, even in a stream with good biological quality. Again, the field situation and proposed EPC values need to be evaluated in more detail to determine if a discrepancy exists.

Future Studies Recommended

Additional research needs to be conducted on EPC and MATE values before they can be used to evaluate and rank pollutants for the purpose of environmental assessment. Much of this work was recommended in the initial MEG document (Cleland and Kingsbury, 1977a) and is now or will soon be in progress. For example, MEG's need to be related to the specific compounds or ionic forms of an element which are most toxic, rather than having a single value represent all compounds and ions which have a common "parent" element. Synergistic and antagonistic effects need to be considered because the may drastically change the hazard ranking of a pollutant in a specific situation. MEG's are also needed for many of the master parameters, such as the "totals" identified by Cleland and Kingsbury (1977a: 155) (e.g., total particulates) or the water quality parameters identified in this study (e.g., pH, suspended solids, dissovled iron, and total organic carbon).

In another vein, the comparison of trace element concentrations in fugitive dust to MEG values points out the need for laboratory and field research, particularly in relation to fugitive dust that consists predominantly of coal particles. First, the rates at which toxic elements leach from coal dust into a variety of soil types need to be explored. Second, the concentrations of toxic elements present in the soil around a large, open coal pile need to be determined when this pile has been in existence for a long period of time. Third, laboratory bioassay and long-term field studies need to be conducted on the effects of coal dust on plants and animals.

It is important that the type of research necessary to improve and expand the initial MEG approach to environmental assessment be completed soon. Once the MEG methodology has been refined it will become an essential part of any assessment of environmental pollution.

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AN OVERVIEW OF CONTROL TECHNOLOGY

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ABSTRACT

An important objective of coal cleaning processes is to reduce the concentrations of pollutants in coal prior to its utilization so that the emissions from utilizing the coal may be reduced. Coal cleaning is an environmental trade-off; that is, the potential pollutants are being transferred from one segment of the environment to another. Through coal cleaning, highly mobile air pollutants which may be discharged by the burning of raw coal may be removed from the cycle as, for example, a solid refuse. But this solid refuse and other wastes generated by cleaning can be important sources of environmental contamination.

As a means of evaluating the full implications of coal cleaning techniques as, for example, a combustion emission control measure, the extent of environmental contamination resulting from coal cleaning technology applications and the control technology for this potential source of contamination needs to be adequately assessed. This paper is a report of progress in quantifying the potential emissions from physical coal cleaning facilities, in evaluating the applicable pollution control technologies for minimizing adverse effects of discharges from these facilities, and in defining and costing these technologies. Needs for and plans for gathering further information are also discussed.

INTRODUCTION

An important objective of coal cleaning is to reduce the concentrations of pollutants in coal prior to its utilization so that the emissions from utilizing the coal may be reduced. Coal cleaning is an environmental trade-off; i.e., the potential pollutants are transferred from one segment of the environment to another. Through coal cleaning, highly mobile air pollutants which may be discharged by the burning of raw coal may be removed from the cycle as, for example, a solid refuse. But this solid refuse and other wastes generated by cleaning can be important sources of environmental contamination.

As a means of evaluating the full implications of coal cleaning techniques as, for example, a conbustion emission control measure, the extent of environmental contamination resulting from coal cleaning technology applications and the control technology for this potential source of contamination needs to be adequately assessed. This paper is a report of progress in quantifying the potential emissions from physical coal cleaning facilities, in evaluating the applicable pollution control technologies for minimizing adverse effects of discharges from these facilities, and in defining and costing these technologies.

TYPES OF PROCESSING AND SOURCES OF POLLUTANTS

Coal preparation plants in general include the functions of (1) size reduction and screening (which may include some separation of impurities from coal), (2) separation of coal from its impurities (in a more sophisticated manner), and (3) dewatering and drying. Table 1 shows the various unit processes that may be employed for coal cleaning while Figure 1 depicts a typical arrangement of unit processes that could be used in a 1000-ton/hour cleaning plant. This figure should provide a common basis and understanding for use in the following discussions.

Size Reduction and Screening

Size reduction and screening are basic and common to all types of coal preparation plants. Some coal preparation plants involve only size reduction and screening functions. A variety of comminution units, primarily crushers and breakers, are employed for size reduction. Screens usually are employed in conjunction with crushers to provide additional sizing of coal. Solid waste produced from crushing nad sizing operations consists of coarse rock and tramp iron. Typically, the amount is less than one percent of the raw coal feed, so that, because of this small amount, it is not a significant disposal problem in comparison with more sophisticated processing operations. Because crushing and sizing is usually a dry process, water pollution potential is limited basically to surface run-off near the plant.

Crushing and sizing of dry coal can be a major source of dust generation. As an air pollutant, coal dust can be classified into two categories based on the particle sizes. The first category consists of relatively large particles (plus 10-micron size range) and is primarily responsible for the environmental hazards of impaired visibility and explosions. These particles tend to settle quickly and thus move out of the air environment much faster than particles of smaller sizes. Furthermore, these particles are readily suppressed by simple water spraying techniques. Consequently, coal dust in the plus 10-micron size range is not normally considered as a serious environmental hazard.

The second category of coal dust consists of minus 10-micron particles and often is defined as respirable dust. Generally, these particles do not impair visibility, but they can be inhaled and affect human respiratory systems. In particular, minus one-micron particles from coal

TABLE 1. UNIT PROCESSES EMPLOYED IN COAL CLEANING OPERATIONS

Size Reduction and Screening
Crushing
Screening
Separation of Impurities
Jigs
Dense Medium Vessels
Air Tables
Wet Concentrating Tables
Dense Medium Cyclones
Hydrocyclones
Froth Flotation
Dewatering and Drying
Mechanical Dewatering
Thermal Drying

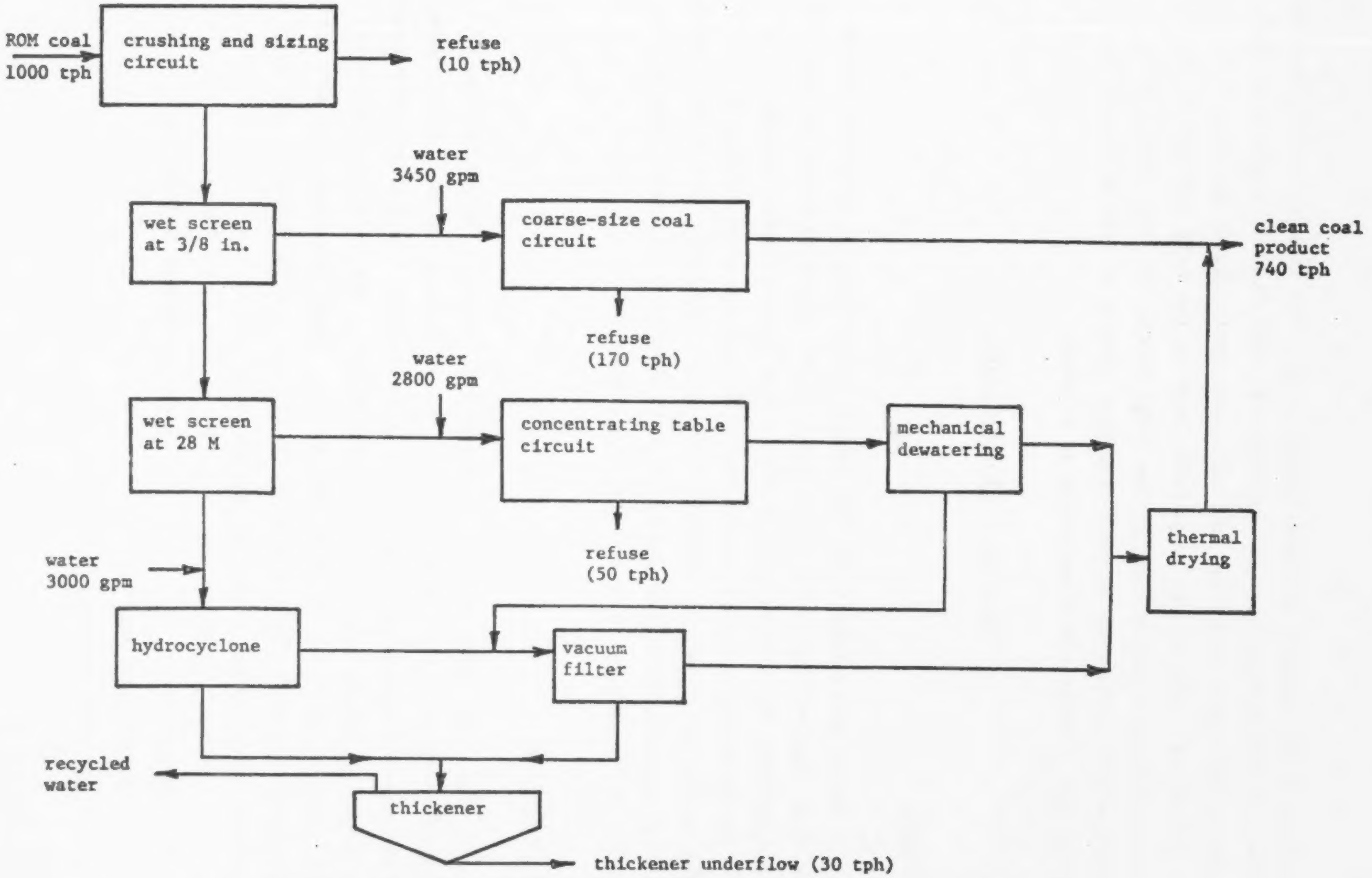

FIGURE 1. FLOW DIAGRAM OF A TYPICAL CONCENTRATING TABLE AND HYDROCYCLONE PLANT HANDLING 1000 TPH OF RAW COAL

are critical with respect to human health (e.g., the inhalation of these small particles is responsible for the occupational lung disease pneumoconiosis). Moreover, these small particles are much more difficult to control than larger particles. Therefore, respirable dust is the main concern in air pollution control. Figure 2 shows the large number of respirable dust particles which is created by coal crushing, giving an indication of the potential for effects which may occur as a result.

Separation of Impurities

Solid Waste

Solid waste resulting from separation processes includes coarse refuse from jigs and dense-medium vessels; fine refuse from air tables, dense-medium cyclones, wet concentrating tables and hydrocyclones; sludge from water clarification circuits; magnetite from dense-medium processes (0.5 lb/ton of feed coal); and chemical reagents from froth flotation processes. These processes, applied to medium and fine-sized feed coal streams, generate on the order of 25 percent of their coal feed as waste.

Water Pollution

The consequence of wet separation of coal is the generation of contaminated water. The characteristics of process water are highly dependent upon the characteristics of coal being processed and the particular process or recovery technique utilized in the operation. The principal pollutant present in process water is suspended solids. Some minerals also are present as dissolved solids. Among the major pollutant constituents or parameters identified in effluents from coal preparation plants are:

Acidity or Alkalinity
Total Iron
Dissolved Iron
Ammonia.
Total Suspended Solids
Total Dissolved Solids
Sulfates

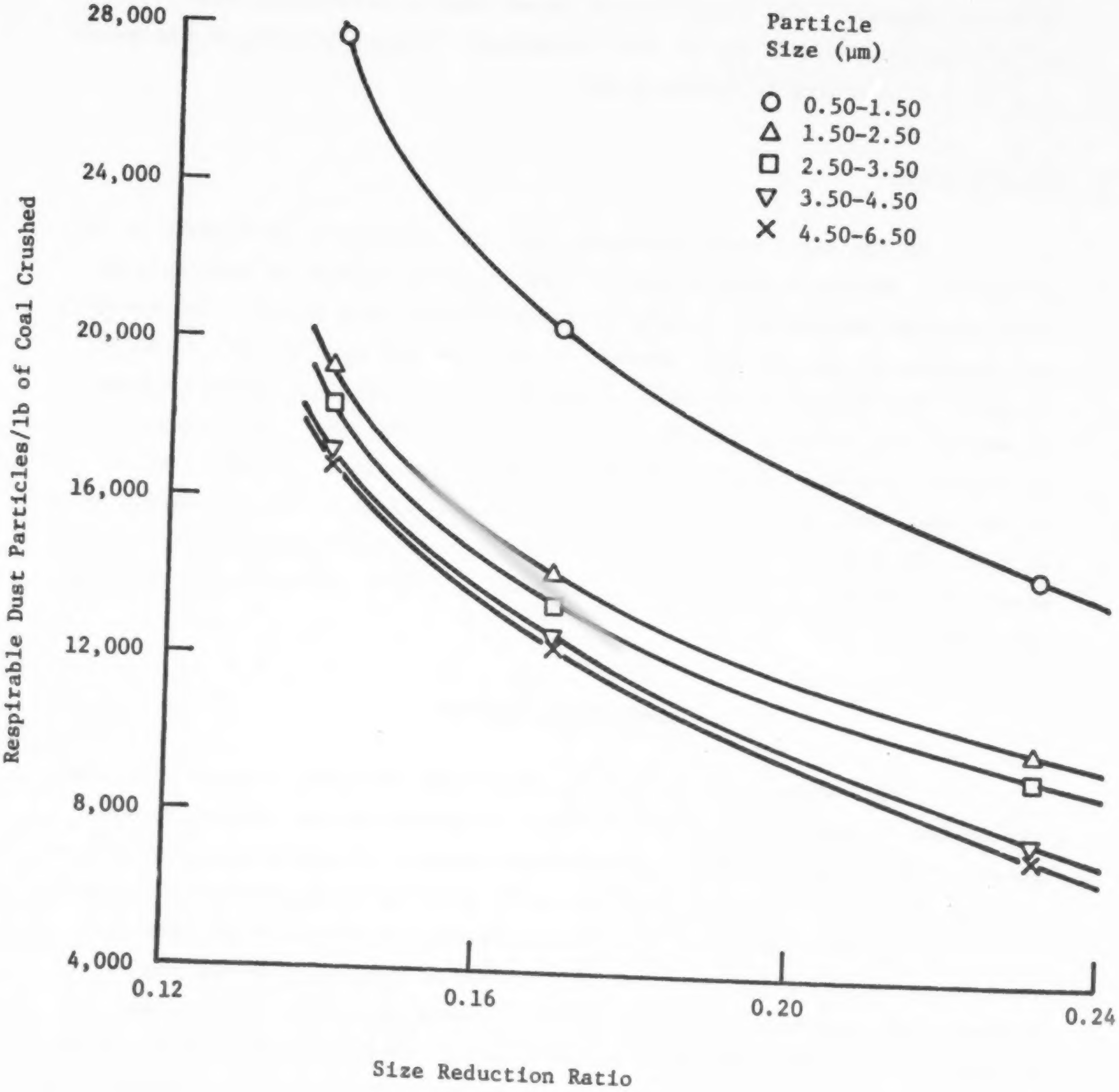

FIGURE 2. AIRBORNE RESPIRABLE DUST GENERATION FROM COAL CRUSHING(1)

Process water from dense media processes may contain magnetite; water from froth flotation operations may contain potentially toxic or noxious chemical reagents. The quantities of water used in processing range from 180 to 1800 gallons per ton of coal processed. A major portion of the water used in coal cleaning is recirculated.

Air Pollution

Of the separation processes, only air tables may contribute to air pollution. Emissions from pneumatic coal cleaning consist of particulates only, because ambient air is used to separate coal from refuse. The quantity and pressure of the air used depends on the size and kind of coal to be cleaned. For pneumatic cleaning of minus 3/8-inch coal, an average volume of exhaust air is about 14,100 cu ft per ton of feed coal. The exhaust air usually picks up about 65 to 70 percent of the minus 48 mesh material in the feed coal, and about 20 percent of minus 3/8-inch coal is smaller than 48 mesh. Therefore, the uncontrolled exhaust air contains about 260 to 280 pounds of dust per ton of feed coal treated or 128 to 138 grains of dust per cubic foot.

Drying and Dewatering

Solid waste from drying and dewatering includes sludges from the air pollution control equipment (usually scrubbers) on the thermal dryers. These scrubbers also generate considerable amounts of contaminated water (lesser amounts, of course, when the usual practice of recirculation is used).

Air emissions from thermal dryers include particulates from the coal being dried and particulates in the form of fly ash from the coal-fired furnace that supplies the drying gases. Gaseous emissions from thermal dryers include carbon monoxide, carbon dioxide, hydrocarbons, sulfur dioxide, and oxides of nitrogen--all furnace combustion products. Table 2 shows typical emission ranges of some of the gaseous emissions. These are the uncontrolled levels and no case is known in which control of SO_2, for example, is exercised. Regardless, the contribution, per ton of coal, to pollutant emissions caused

TABLE 2. GASEOUS EMISSIONS FROM THERMAL DRYERS(2,3)

Pollutant	Emission Rate, lb/ton of coal dried	Concentration, ppm
NO_2	0.2	40 to 70
SO_2	0.38 x (%S)	0 to 11.2
CO	0.03	50
Hydrocarbons as methane	0.01	20 to 100

by coal drying is very small in comparison to the total emissions produced subsequently during the burning of the clean coal product.

Coal Storage, Handling, and Transportation Operations

Storage of coal is an economic necessity in coal preparation. It provides a reserve against production interruptions and also facilitates intermittent shipment. Coal is stored in open piles or enclosed bins and silos. Transportation of coal from mines or preparation plants to the point of consumption is one of the most important factors affecting coal utilization. Transportation modes are rail, waterway, truck, pipeline, and belt conveyor. In conjunction with the transportation and storage of coal, a wide variety of material handling operations is needed. This includes loading and unloading, stacking and reclaiming, and transferring coal in a plant.

Water Pollution

Outdoor coal piles have very large surface areas, and coal residence times in them are relatively long so that rainwater has a chance to react, form acids, and extract sulfur compounds as well as soluble metal ions. Coal pile leachate is generally similar to acid mine drainage. The quantity of coal pile leachate is highly variable, both in an absolute sense and with time. It depends upon the topography and drainage area of the coal pile site, the configuration and the volume of the stock pile, and the type and intensity of precipitation. Table 3 shows a typical composition of coal pile drainage. Its composition is not much different than acid mine drainage. Obviously, then, control and treatment of this drainage must be exercised for proper protection of the environment to be achieved.

In addition to the coal pile leachate, accidental spills from barge transport and coal slurry pipelines may produce serious water pollution problems; however, no relevant quantitative data covering these situations have been found in the literature.

TABLE 3. TYPICAL COMPOSITION OF DRAINAGE FROM COAL PILES(4)

	Concentration, mg/l*
Alkalinity (as $CaCO_3$)	15 - 80
BOD	3 - 10
COD	100 - 1,000
Total solids	1,500 - 45,000
Total suspended solids	20 - 3,300
Total dissolved solids	700 - 44,000
Nitrate	0.3 - 2.3
Phosphorus	0.2 - 1.2
Total hardness (as $CaCO_3$)	130 - 1,850
Sulfate	130 - 20,000
Iron	0.4 - 2.0
pH	2.2 - 8.0

*Except pH

Air Pollution

The principal air pollutant from storage, transportation, and handling of coal is fugitive coal dust. This dust has the particle size distribution characteristics shown in Table 4. The amount of dust generated varies widely, depending on such factors as climate, topography, and characteristics of coal, including moisture content. Thus, for example, the handling of thermally dried coal would result in the generation of more dust than would be generated with undried coal. It is estimated that as much as about 80 pounds of coal per ton hauled are lost as fugitive dust during the transport and handling operations. A dust emission factor from coal storage piles has been estimated to be equal to approximately 0.00118 lb/ton-year (0.59 mg/kg-yr).

Coal Waste Disposal Areas

Coal refuse consists of waste coal, slate, carbonaceous and pyritic shales, and clay associated with a coal seam. It varies considerably in physical and chemical characteristics, depending on both its source and the nature of the preparation process. It is estimated that about 25 percent of raw coal mined is disposed of as waste. Over 3 billion tons of solid waste have accumulated in the United States, and the total number of active and abandoned coal waste dumps is estimated to be between 3000 and 5000. About one-half of these pose some type of health, environmental, or safety problem.

Water Pollution

The weathering and leaching of coal refuse dumps produces several types of water pollution. These include silt, acids, and other dissolved mineral matter. Pollution from coal waste dumps is similar to that from surface mines; i.e., waste water from a refuse disposal area can continue indefinitely to pollute after the disposal has ceased, and volumes of waste water are highly dependent on precipitation and surface water flow patterns.

TABLE 4. PARTICLE SIZE DISTRIBUTION OF AIRBORNE COAL DUST(5)

Particle Radius Range, (μm)	Mean Particle Radius, (μm)	Weight Percent	Rate of Settling, (m/sec)
< 3	2	2	0.0005
3-6	4	3	0.002
6-15	9	21	0.012
15-30	20	30	0.047
> 30	50	44	0.247

Siltation from coal refuse dumps is caused by finely divided coal, minerals, and discarded soil. Acid drainage is produced when iron sulfides are exposed to air and water. Acid drainage is one of the most serious water pollution problems in many parts of the U.S. In Appalachia alone, more than 10,000 miles of streams are affected by acids from coal mines and refuse dumps.

Air Pollution

Burning refuse piles present a difficult air pollution problem. The oxidation of residual coal or other mineral matter in coal refuse piles can produce sufficient heat to ignite the interior of the pile. These burning wastes emit fumes including carbon monoxide, sulfur oxides, and hydrocarbons. Some waste piles have been burning continuously for over 20 years, and approximately 300 coal waste piles are still burning.

CHANGES IN DISTRIBUTION OF POLLUTANTS

Recently, the fate of potentially toxic elements in coal during coal cleaning has received special attention. Coal has been found to contain nearly every naturally occurring element. Coal cleaning affects the distribution of these elements between clean coal and refuse portions. Table 5 shows the concentrations of a few selected elements in raw coal, clean coal at 75 percent weight recovery, and in the resulting refuse. The enrichment factor is defined as the concentration of an element in the clean coal (or in the refuse) divided by the concentration of the same element in raw coal. Of 29 elements measured in this way by the Illinois State Geological Survey, all but boron and germanium had higher concentrations in the refuse than in the raw coal. Beryllium is distributed approximately evenly between the clean coal and the refuse.

Reduction of trace elements is an added benefit of coal cleaning for reducing the environmental pollution from burning coal; hwoever, the concentration of trace elements in the solid waste may increase the potential for environmental contamination from this source. These materials can be

TABLE 5. ENRICHMENT FACTORS IN FLOAT-SINK SEPARATION OF ILLINOIS COALS(6)

Element	Concentration, ppm (unless otherwise stated) Raw Coal	Clean Coal	Refuse	Enrichment Factor Clean Coal	Refuse
S	4.4 %	1.6 %	12.9 %	0.36	2.93
As	11.5	1.5	41.0	0.13	3.57
Be	3.0	2.9	3.3	0.97	1.10
Ge	6.7	8.1	2.3	1.21	0.34
Se	2.8	1.3	7.3	0.46	2.61

subjected to leaching by rainwater or surface flows that could produce water pollution problems. In addition, under certain conditions, burning refuse piles could discharge some of these elements into the atmosphere. Hence, the environmental consequences of solid refuse disposal should be carefully assessed.

AIR POLLUTION CONTROL TECHNIQUES

Several types of air pollution control devices are available for application to coal cleaning operations. In choosing a particular technique for application, the factors listed in Table 6 must be considered. The choice of the control device depends also on the type of pollutant (particulate or gaseous); the properties of the pollutant (such as size, density, and shape for particulates, and equilibrium solubility, reactivity, and adsorptivity for gases); and the properties of the conveying medium (such as density, temperature, and velocity). Particulate control devices may be broadly classified as dry inertial collectors (gravity settling chambers and cyclones), filters, wet scrubbers, and electrostatic precipitators. Electrostatic precipitators are not used at coal cleaning plants because of the explosive nature of coal-dust-air mixtures and the charged field in the precipitator. Control devices for the removal of gases or vapors involve adsorption or absorption in a variety of contacting devices. Table 7 lists the mechanisms and types of equipment in common use today for the removal of the two basic air pollutant types.

Particulate Control Devices

Dry Inertial Collectors

Dry inertial collection systems utilize either gravitational or inertial forces to separate the particulates from the gas stream. The collection systems are characterized by moderate removal efficiencies, low energy requirements, low capital and operating costs, and an ability to accommodate high inlet dust loadings and operate at high temperatures. For applications at

TABLE 6. FACTORS FOR EVALUATION OF AIR POLLUTION CONTROL TECHNIQUES

(1) Characteristics of air emissions and operational constraints

(2) Control technology removal efficiency

(3) Capital and operating costs

(4) Disposal of wastes

TABLE 7. LISTING OF AIR POLLUTION CONTROL EQUIPMENT

Control of Particulates	Control of Gases and Odors
Dry Inertial Collectors	Dry Adsorbers
Gravity Settling Chambers	Wet Absorbers
Cyclones	
Fabric Filters	
Electrostatic Precipitators	
Wet Inertial Scrubbers	
Impingement	
Centrifugal	
Venturi	
Self-Induced	

coal cleaning plants, the inertial collectors are used primarily as scalping units or precleaners to remove the major volume of particulates from pneumatic cleaner and thermal dryer off-gases. To meet the particulate emission standards, the collectors are generally followed by more efficient removal devices, such as high-energy scrubbers or filters.

Fabric Filters

Fabric or bag filters are regarded as one of the simplest and most reliable high-efficiency dry collector devices, being capable of 99.9 percent removal of submicron size particles. They are suitable for a wide variety of dry particulate removal applications and, depending on the type of fabric selected, are resistant to chemical and mechanical rigors and are operable at moderately high temperatures.

Wet Inertial Scrubbers

Wet scrubbers or collectors utilize a liquid, generally water, to assist in removing the dust particles from the gas stream. The major features that make wet collectors popular dust control devices are their high removal efficiencies, ability to remove gaseous pollutants, tolerance of moisture in the gas, and relatively low capital costs. Disadvantages inherent with wet collectors in general include the following: (1) the captured particulate is in the liquid state and sometimes presents a water or waste disposal problem, (2) the scrubber internals are subject to plugging and corrosion, (3) the scrubbed gas is saturated with the liquid vapor, and (4) the energy requirements for some units are high, which results in higher operating costs than for some dry collectors. Four types of the more common types of wet collectors used for particulate control are the impingement, centrifugal, venturi, and self-induced spray scrubbers.

Evaluation of Particulate Collection Devices

On the basis of the characteristics outlined for the three major emissions from coal cleaning unit operations and the performance evaluation of the control equipment, those equipment types most appropriate as control equipment for each major emission may be selected. The appropriate control selections are presented in Table 8.

Gaseous Removal and/or Collection Devices

Gaseous removal and/or collection devices are designed to extract specific gaseous compounds from a carrier gas stream. Although not practiced to date, the major potential application of gaseous removal devices in coal cleaning operations is for the removal of SO_2 from thermal dryer off-gases. To this end, two major types of gaseous removal processes, dry adsorption and wet absorption, can be considered for controlling sulfur dioxide emissions. Both processes have achieved commercial status in flue gas desulfurization for utility and industrial boilers. They are not, however, efficient dust removal devices, and, to meet particulate control regulations, they must be used in conjunction with or preceded by a high-efficiency wet scrubber.

Dry Adsorbers

Removal of sulfur dioxide from flue gas or drier off-gas may be accomplished by either molecular sieves or carbon adsorption. Unfortunately, molecular sieves have a greater affinity for water than for SO_2, and since water in flue gas or drier off-gas is present in considerably greater concentrations than SO_2, the sieve is rendered essentially ineffective unless preceded by a drying device, i.e., another sieve.

Wet Absorbers

Absorption is regarded as the most developed method for removing SO_2 from flue gases, and, to date, several hundred various commercial-size installations have been applied worldwide to utility and industrial boilers.

Several different types of absorption equipment are utilized to effect contact of the gas with the scrubbing slurry; some of the more common types are spray towers, venturi scrubbers, and marble bed scrubbers. A variety of different aqueous solutions are also utilized to capture the SO_2.

TABLE 8. SUMMARY OF APPLICATIONS FOR PARTICULATE CONTROL EQUIPMENT

Emission Source	Typical Characteristics of Dust	Appropriate Control
Crushing and Sizing Operations	Dry, submicron up to about 6 microns in size; light dust load, ambient temperature	Cloth filters or high-energy wet scrubbers
Pneumatic Cleaners	Dry, submicron up to 48 mesh in size, heavy dust load (>100 gr/dscf), ambient temperature	Primary cyclone-cloth filter or primary cyclone-high-energy wet scrubber
Thermal Dryer	High humidity, submicron up to about 100 microns in size, heavy loadings up to 200 gr/dscf, temperature 200 to 250 F.	Primary cyclone-high efficiency wet scrubber

They may be classified into four different categories: slurry solutions, clear solutions, weak acid solutions, and organic liquids. The most developed systems to date are those utilizing slurry solutions in spray towers or venturi scrubbers.

WATER POLLUTION CONTROL TECHNOLOGY

Process and scrubbing water effluents from coal cleaning operations contain two types of pollutants: suspended materials (solid or liquid) and dissolved substances. The technology available for removing suspended materials from the water includes mechanical dewatering, sedimentation, and flotation. Dissolved substances can be removed from water or converted to less objectionable forms by neutralization, adsorption, ion exchange, reverse osmosis, freezing, or biological treatment. Table 9 lists the methodologies currently in use or contemplated for use in treating coal cleaning wastewaters. While all of the techniques for control of suspended materials have found application, there is no known evidence of attempts at application of techniques such as ion exchange, reverse osmosis, or freezing for control of dissolved materials.

Control of Suspended Materials

Suspended solids may be removed from liquid streams by mechanical dewatering methods, sedimentation, or flotation. Each of these methods produces a solid material which may be processed further in the coal cleaning plant, in the case of a coal-rich material, or disposed of as solid waste.

Mechanical Dewatering

Mechanical dewatering devices applicable for removing solid materials from water include centrifuges and various kinds of filters. A centrifuge is a device which rapidly rotates a solids-containing stream in order that centrifugal force can separate the solid and liquid fractions. Vacuum filters are used in the dewatering of fine coal products and fine refuse from wastewater.

TABLE 9. CLASSIFICATION OF WATER TREATMENT TECHNOLOGIES

Control of Suspended Materials	Control of Dissolved Materials
Mechanical Dewatering	Neutralization
Centrifuges	Adsorption
Cyclones	Ion Exchange
Screens	Reverse Osmosis
Filters	Freezing
Sedimentation	Biological Oxidation
Settling Ponds	
Sedimentation Tanks (Thickeners)	
Inclined Plate Settlers	
Flocculation	
Flotation	

Although a drum type of vacuum filter is available, the disk type has been the traditional choice in coal cleaning plants.

Sedimentation

Sedimentation processes allow suspended materials to settle to the bottom of a vessel and incorporate means for continually removing settled solids and supernatant liquor separately. Systems classified under sedimentation include settling ponds or lagoons and various configurations of sedimentation tanks.

Filtration and sedimentation can be improved by the addition of flocculants. Among commonly used additives are alum, lime, iron salts, sulfuric acid, starches, and polymers. Although polymers are the most expensive, on a per unit basis, they are used in very small concentrations and work very well.

Control of Dissolved Materials

The most common pollution problem with dissolved substances in wastewater is pH control. For coal cleaning wastewater and drainage from coal and refuse piles, the problem is usually acidity, so an alkaline additive is needed; lime is the preferred reagent for this purpose.

SOLID WASTE CONTROL TECHNOLOGY

Primary Problems with Refuse Disposal Areas

The major problem areas associated with land disposal of coal cleaning refuse are fugitive dust, fire potential, erosion, and leachate generation. Aesthetics and the ultimate use of the disposal area are generally less difficult problems to solve.

The refuse generated by a coal preparation plant contains considerable quantities of fine particles, leading to potentially serious fugitive dust problems. Proper disposal site selection can be a partial solution to this problem. The orientation of the valley with respect to prevailing winds should be considered. A crusting agent may be employed to prevent water infiltration and fugitive dust from refuse piles.

Because of the considerable amount of organic matter in coal preparation refuse, fire resulting from spontaneous combustion in the refuse banks is a matter of concern. Compacting the refuse piles will minimize air circulation and reduce the likelihood of fire. In addition, sealing the pile, either with an occasional soil covering or with a crusting agent, also may reduce the fire potential.

Particle sizes are such that the refuse is particularly susceptible to erosion. Diversion ditches to minimize flow of water over the refuse surface, as well as siltation basins to capture eroded material, are essential. The supernatant liquid (leachate) from the siltation basin should be monitored for high pH, sulfate, calcium, total dissolved solids, and heavy metals before being discharged to the environment. Treatment of this liquid may be necessary.

Because of the heavy metals concentrated in coal refuse, the leachate from the refuse can be expected to be high in metal ions. This is especially true if the leachate is acidic, as most of the metallic minerals are quite soluble in acid.

It is possible to minimize leachate production from a disposal facility by (1) diverting all surface drainage, (2) applying a cover material to prevent infiltration of rainfall, (3) grading to promote rapid runoff (but not so rapid as to create excessive erosion), (4) minimizing the open (working) area, and (5) applying a vegetative cover upon completion of an area. In most cases, a naturally impermeable soil, or in some cases a synthetic liner, is used to prevent infiltration of the leachate into the ground and eventually into the groundwater.

An underdrain system is needed to gather the leachate and carry it to a leachate treatment system. Leachate treatment will probably consist of lime neutralization and settling. As well as improving pH, lime treatment will remove large quantities of metal ions, which are relatively much less soluble at higher pH levels. However, additional physical or chemical treatment may be required.

Fine Refuse Disposal

Fine refuse is considered to be refuse smaller than 28 mesh. It occurs as the thickener underflow and may contain 75 percent moisture. Therefore, handling of fine refuse is generally done hydraulically, by pumping the slurry from the preparation plant to a disposal area. Direct disposal of the fine slurry into streams is no longer practiced. Disposal of fine refuse is now accomplished by slurry impoundment or dewatering, allowing the resulting fine solids to be disposed of together with the coarse refuse.

POLLUTION CONTROL COSTS ASSOCIATED WITH COAL CLEANING

With the use of proper control methods and "good housekeeping", environmental control is technically feasible for most waste streams emanating from coal preparation plants. However, the question is: "What is practical and to what extent does one have to go to provide an acceptable discharge to the environment?" Moreover, the costs of pollution control for coal preparation (including recovery and reclamation) are frequently so great that only a minimal effort is made to control pollution.

In the following discussion, the costs for various types of pollution control equipment and techniques have been summarized from Battelle cost estimates and from other sources.

Air Pollution Control Equipment

Table 10 shows the installed capital costs and operating costs for air pollution control equipment for a hypothetical 1000 tons/hr coal cleaning plant with the following levels of treatment.

(1) Crushing and Sizing

(2) Medium Size Coal Beneficiation With Air Tables

(3) Fine Size Coal Beneficiation With Thermal Drying

For the first two types of treatment, more than one particulate control device is applicable; in this case, cost estimates are shown for

TABLE 10. ESTIMATED COSTS OF AIR POLLUTION CONTROL EQUIPMENT FOR TWO TYPES OF 1000 TPH COAL CLEANING PLANTS(7,8,9)

Plant Type(a)	Emission	Applicable Control Equipment	Installed Cost of Control Equipment, Dollars (1977)/ton/hr	Annual Operating Cost of Control Equipment(b), cents/ton
1,2	Dust from crushing and sizing operation	Dust enclosures with dry bag collectors	36	0.1
		Dust enclosures with high-efficiency wet scrubbers	20	0.2
1	Dust from air tables operating on medium-size coal	Primary cyclones followed by dry bag collectors	360	2.8
		Primary cyclones followed by high-efficiency wet scrubbers	200	9.7
2	Thermal dryer off-gas	Primary cyclones with high-efficiency wet scrubbers	250	12.2
		Primary cyclones with high-efficiency wet scrubbers followed by limestone scrubbing	9250	93.8

(a) Both plant types 1 and 2 include crushing and sizing operations and coarse (3 x 3/8 inch) coal beneficiation by jigs or dense medium vessels. Plant type 1 includes pneumatic tables for medium (3/8 inch x 28 M) and fine (28 M x 0) coal beneficiation. Plant type 2 includes wet concentrating tables or dense medium cyclones for medium size coal beneficiation and hydrocyclones or froth flotation for fine coal beneficiation.

(b) Excludes capitalization, depreciation, and interest. Based on 180 (2-shift) days.

each type of treatment. For the third type, an additional cost was included to account for flue gas desulfurization on the thermal dryer. Limestone scrubbing was selected as the basis for the cost estimate because of its more developed state.

To more effectively assess the environmental problems associated with disposing of the collected particulate wastes generated from the crushing and sizing operations, information should be obtained on the characteristics of the wastes. Knowledge of the composition, leachability and chemical activity of the wastes would be helpful in determining any potential environmental complications with their disposal as well as alternative handling or disposal procedures.

The capital and operating cost information should be better quantified to determine more accurately pollution control costs for different types of plants. In addition to more accurate modular costs, information is also needed on instrumentation and control, installation, power, and maintenance costs.

Water Pollution Control Equipment

Table 11 shows the estimated costs of water pollution control equipment for a hypothetical 1000 tons/hr coal cleaning plant with the following specified processing configurations:

(1) Crushing and sizing with dry screening and wet beneficiation

(2) Medium size coal beneficiation with wet screening and wet beneficiation.

In generating the treatment costs, it has been assumed that all water treatment is performed to satisfy environmental constraints. Actually, much of the treatment, particularly the dewatering treatment, is necessary for operation of the coal cleaning processes. Thus, a portion of the costs cited may be attributed to process requirements rather than environmental requirements. Furthermore, since the use of closed water circuitry is a viable alternative to treatment and release of wastewater, the water most likely to be treated for release to the environment is runoff and leachate from coal storage and coal refuse piles.

TABLE 11. ESTIMATED COSTS OF WATER POLLUTION CONTROL EQUIPMENT FOR SELECTED 1000 TPH COAL CLEANING PLANTS(10)

Plant Type	Effluent	Quantity, gpm	Applicable Control Equipment	Installed Cost of Control Equipment, 1977 dollars	Annual Operating Cost of Control Equipment,(b) 1977 cents/ton
Crushing and Sizing with Dry Screening and Wet Beneficiation	Process Water Flow–Suspended Solids	3,450	Radial flow thickener	345,000	0.8
			lagoon, or	108,000	0.6
			froth flotation	33,000	0.7-1.4
	Dissolved Solids		Absorption-activated carbon treatment	1,700,000(a)	2.0
Crushing and Sizing with Wet Screening and Wet Beneficiation	Process Water Flow–Suspended Solids	7,650	Mechanical dewatering–hydroclones,	150,000	1.4
			microscreens, or	230,000	1.0
			pressure filters	310,000	1.8
			Thickener or	510,000	1.2
			lagoon	160,000	0.8
Fine Size Coal Beneficiation with Hydroclones and Thermal Drying	Process Water Flow–Suspended Solids	9,250	Radial flow thickener	560,000	1.3
			or lagoon	180,000	0.9

(a) Adsorption is not presently used to treat coal cleaning process water, and would not be necessary for treating the recirculating process water for any plant with a closed water circuit.

(b) Including depreciation and interest on capital.

Much of the information presented is based on preliminary information and estimates. Contact with plant operators and vendors can aid in acquisition of much more detailed capital and operating costs of control equipment, especially as applied to the specific plant types. More information should be acquired on disposal of waste streams produced by ion exchange and reverse osmosis treatments. The data acquisition task eventually will provide detailed information on performance of control equipment and actual pollutant concentrations in raw and treated water streams. In addition, the proportions of treated and untreated process water will be discovered, making it possible to estimate real pollution control costs more accurately.

Solid Waste Disposal and Reclamation

The U.S. Bureau of Mines has studied the costs to the coal industry of refuse disposal and reclamation for nine coal waste disposal projects. These cost estimates are the basis for the costs shown in Table 12. Waste disposal costs are divided into those for transportation of the waste to the disposal plant, spreading and compacting the wastes, soil covering and planting of the disposal area, and capital costs for land, site preparation, and operating equipment. These costs did not include the cost of installing or operating leachate collection or surface drainage collection and treatment facilities, which will increase the total costs.

TABLE 12. ESTIMATED COSTS OF SOLID WASTE DISPOSAL FOR TYPICAL 1000 TPH COAL CLEANING PLANT(11)

Transportation of refuse to disposal site	$0.36/ton refuse
Spreading and compaction of refuse	0.17/ton refuse
Soil covering and planting	0.05/ton refuse
Capital cost	0.04/ton refuse
	$0.62/ton refuse

The costs are presented here in terms of dollars per ton of refuse. This total compares with results of a study done by the University of Kentucky(12) showing coal refuse disposal costs in the range of \$0.50 to \$1.00 per ton. Based on a typical coal cleaning plant, such as the concentrating table and hydrocyclone plant shown earlier, with a rejection of 26 percent of raw coal input, the total cost shown here amounts to \$0.22 per ton of clean coal or \$0.16 per ton of raw coal input.

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CHARACTERIZATION OF PREPARATION PLANT WASTEWATERS

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ABSTRACT

During the Environmental Protection Agency's review of guidelines for the coal mining industry, eighteen preparation plants and ancillary areas were screened for priority pollutants as well as the classical ones. Of these eighteen, four were examined more extensively in the "verification" phase of the review. This paper discusses the findings of those studies. The compositions found in the screening phase are compared with those from the verification phase. Differences in composition among preparation plants are compared on the basis of region, rank of coal, type of mining, cleaning process, and plant age. By way of presenting these results, sampling and analysis procedures are discussed.

INTRODUCTION

In December of 1976, the Effluent Guidelines Division of the Environmental Protection Agency commissioned a study by Versar to provide technical assistance in reviewing the best available technology (BAT) for wastewater pollutants from the coal mining point source category. This review resulted from a federal court decision of June 7, 1976, which required the Agency to perform sampling and analysis of wastewaters from 21 industries for certain pollutants as well as classical water quality parameters. The above pollutants represent 65 compounds and classes of compounds which the EPA had failed to take into consideration in previous effluent guidelines studies. The process of delineating specific compounds from these classes resulted in a list of 129 organic compounds and metals which are tabulated in Appendix A and have become known as the priority pollutants.

The screening sampling phase of this study was conducted during April, May and June of 1977. Eighteen preparation plants, associated with coal mines were visited and wastewater samples were obtained from 7 of these facilities. In addition, wastewater samples were obtained from such ancillary areas as refuse piles from 5 of these facilities.

Four coal preparation facilities currently are being examined more extensively during the verification phase of this review. Verification sampling was to have been conducted this past spring. However, the recent strike by the United Mine Workers of America delayed the scheduling of this phase of the program.

In the interim, Versar has been conducting a mine drainage treatability study at the Environmental Protection Agency Crown Mine Drainage Control Field Site facility, located near Morgantown, West Virginia. The study is designed to identify and assess control technologies to remove organic priority pollutants found in coal mine drainage and preparation plant wastewaters. Preliminary findings from this study are also discussed in this paper.

DISCUSSIONS OF METHODOLOGY

Site Selection

Twenty-three coal mining facilities were selected for screening sampling by Versar in conjunction with the Environmental Protection Agency and the Water Quality Committee of the National Coal Association. Facilities were selected on the basis of region, rank of coal, type of mining and cleaning process. Versar conducted the sampling at 22 mines. The remaining facility was sampled by the Calspan Corporation. Gail Goldberg was the first project officer on this program, succeeded by Al Galli, who, in turn, was followed by the current project officer, Ron Kirby. This work was under the direction of Bill Telliard, Chief, Energy and Mining Branch, Effluent Guidelines Division, EPA, under contracts 68-01-3273, Task 15 and 68-01-4762.

Outfall Identification

Raw wastewater and treated effluents were sampled at each facility, where mining or preparation process design permitted. Continuous discharges were sampled by time proportional composite. Where discharges or flows were intermittent, because of the dry weather conditions of the spring of 1977, grab samples were taken and composited, where possible.

Sampling Methods

Continuous discharges were composite sampled for 24 hours using an "Isco" sampler.* Intermittent discharges were grab composited. Composite samples were divided into 1 liter aliquots for analyses for metals, organics, pesticides, solids, asbestos, phenols, TOC and COD. Separate samples were collected for volatile organics and cyanide analyses. All samples were stored, preserved and shipped according to "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," USEPA, EMSL, Cincinnati, Ohio 45268, April 1977. The pH was measured using an Orion or Cole Palmer pH meter. Flow rates were determined by methods appropriate to the specific situation.

Analytical Methods

Analyses were conducted by Versar, the EPA Region V Analytical Laboratory and two EPA analytical contractors. Versar conducted the analyses for the classical water quality parameters as well as for phenols, cyanides, pesticides, PCBs and four priority metals: antimony, arsenic, selenium and thallium. The remaining metals were analyzed by the EPA Region V Analytical Laboratory in Chicago. The Carborundum Corporation and Gulf South Research, Inc., analyzed the samples for organics.

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* Isco - Instrumentation Specialties Company, Lincoln, Nebraska

All analyses were conducted according to EPA analytical protocols. Metals were analyzed by plasma source atomic absorption spectrophotometry. Organic compounds were identified using gas chromatography/mass spectroscopy (GC/MS).

RESULTS AND DISCUSSION

The results of the screening phase of this program are presented in two parts: metals and organics. These parts are further broken down into waters from preparation plants and water from associated areas, i.e., refuse and storage piles. These results are further subdivided and regrouped by the mine type (surface or deep), the mine water (acid or alkaline), type of processing (water only, heavy media and flotation), geographical location and water treatment process. These results are discussed as they are presented.

Since these are the results of the screening phase, they are somewhat preliminary in nature in that they have not been verified by more extensive sampling. Furthermore, the coal mining industry was the first to be sampled under the BAT review, and thus was the first industry to be sampled for many of these parameters. This is especially important in considering the organic priority pollutants.

In the following, the terms acid preparation plant and alkaline preparation plant are used. These refer to the type of drainage associated with the mine that supplies the coal to the plant and not necessarily to the water from the plant itself. However, preparation plants in the acid group do have generally lower pH waters than those in the alkaline group - 3.8 vs. 7.0.

Priority Metals

Table 1 shows that virtually all priority metals (except silver) were found in the wastewaters from acid plants. This may be contrasted with the results for alkaline plants shown in Table 2. In the acid case, three metals were found in all streams, and four metals were found in eight of the nine streams. However, in the alkaline case, no metal was found in all streams, and only the "ubiquitous" iron was found in all but one stream. Only for one metal, chromium, was the highest concentration found in an alkaline plant. Clearly then, the waters associated with preparation plants processing coal from alkaline mines are "cleaner" than waters from those plants cleaning coal from acid mines.

The kind of stream that produces the highest concentration of these metals is shown in Table 3 for each priority metal. Note that the high concentrations occur in three streams out of the nine sampled. These are:

(1) A refuse slurry from an anthracite breaker,
(2) A grab sample taken from a drag tank,
(3) A very acid, old, strip pit used for a recycle pond.

In two of these cases samples were taken of the same waters after treatment. These treated values are shown in Table 4 along with the percent reduction in concentration.

In the first case, the anthracite breaker, the treatment consisted of a series of three settling ponds. The first two were divided by a baffle dam constructed of refuse. The second of these emptied, by means of an asbestos pipe, into a third pond.

The second case, the drag tank water, combines with other circuits in the prep plant and flows to a slurry pond from where it is recycle to the process.

The third case, the very acid pond, is unique. This was a non-discharging pond which was an old acid strip pit. This water was so acid, pH 2.9, that it had to be neutralized before reuse. This was accomplished by injecting anhydrous ammonia in the recycle line. This line could not be sampled readily to assess the effectiveness of the treatment, however, the treatment may account for the high levels of nickel and zinc as the ammonium

TABLE 1

ACID PREPARATION PLANTS, PRIORITY METALS FREQUENCY AND RANGE

Metal	Frequency (9 Streams)	Range, (mg/l) Low	Range, (mg/l) High	Detectability Limit, (mg/l)
Antimony	8	0.001	0.021	0.001
Arsenic	9	0.002	1.23	0.001
Beryllium	2	0.007	0.02	0.002
Cadmium	1	—	0.032	0.02
Chromium	5	0.036	0.44	0.024
Copper	8	0.03	0.72	0.004
Iron*	9	0.098	3,000	0.02
Lead	4	0.067	0.76	0.06
Manganese*	9	0.025	39	0.01
Mercury	6	0.0003	0.0075	0.0001
Nickel	3	0.095	0.92	0.05
Selenium	8	0.005	0.41	0.006
Silver	0	—	—	0.025
Thallium	6	0.001	0.070	0.001
Zinc	8	0.039	1.37	0.025
Cyanides	0	—	—	0.005
Phenols	1	—	0.025	0.02

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* Not on the priority pollutant list but one on which the industry is regulated

TABLE 2

ALKALINE PREPARATION PLANTS, PRIORITY METALS FREQUENCY AND RANGE

Metal	Frequency (10 Streams	Range, (mg/l)		Detectability Limits, (mg/l)
		Low	High	
Antimony	5	0.002	0.007	0.001
Arsenic	7	0.002	0.045	0.001
Beryllium	0	—	—	0.002
Cadmium	0	—	—	0.02
Chromium	5	0.033	2.0	0.024
Copper	3	0.005	0.27	0.004
Iron*	9	0.161	200	0.02
Lead	0	—	—	0.06
Manganese*	8	0.024	2.0	0.01
Mercury	6	0.0004	0.002	0.0001
Nickel	1	—	0.53	0.05
Selenium	4	0.002	0.05	0.001
Silver	0	—	—	0.025
Thallium	4	0.001	0.004	0.001
Zinc	8	0.026	1.0	0.025
Cyanides	0	—	—	0.005
Phenols	1	—	0.035	0.02

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* Not on the priority pollutant list, but one on which the industry is regulated

TABLE 3

SOURCE OF ACID PREPARATION PLANT MAXIMUM CONCENTRATIONS

Metal	Maximum Concentration	Stream Description
Antimony	0.02	Prep plant drag tank, grab sample, total metal
Arsenic	1.23	Anthracite refuse slurry, total metal
Beryllium	0.02	Slurry to thickener grab sample
Cadmium	0.032	Very acid recycle pond (pH 2.9), actually an old strip pit
Chromium	0.44	Drag tank, grab sample
Copper	0.72	Anthracite refuse slurry
Iron	3,000	Drag tank
Lead	0.76	Anthracite refuse slurry
Manganese	39	Very acid recycle pond (pH 2.9)
Mercury	0.0075	Anthracite refuse slurry
Nickel	0.92	Very acid recycle pond
Selenium	0.41	Anthracite refuse slurry
Silver	—	None detected
Thallium	0.07	Drag tank grab sample
Zinc	1.37	Very acid recycle pond
Cyanides	—	None detected
Phenols	0.025	Anthracite refuse slurry

TABLE 4

EFFECT OF TREATMENT ON HIGH CONCENTRATIONS

	Concentration, (mg/l)		Reduction (percent)
Metal	Raw	Treated	
Antimony	0.021	0.001	95.4
Arsenic	1.23	0.004	99.7
Beryllium	0.02	(a)	—
Cadmium	0.032	(b)	—
Chromium	0.44	0.036	91.8
Copper	0.72	0.044	93.9
Iron	3,000	0.183	99.994
Lead	0.76	<0.06	>99.9
Manganese	39	(b)	—
Mercury	0.0075	0.0016	78.7
Nickel	0.92	(b)	—
Selenium	0.41	<0.006	>98.5
Thallium	0.070	<0.001	>98.6
Zinc	1.37	(b)	—

(a) Treated water not sampled

(b) Closed circuit, pond does not discharge complexes. (The latter has not been verified by any analyses and is offered only as a possible explanation.)

The extraordinary effectiveness of settling in these two cases leads to the conclusion that the priority metals are associated primarily with the solid phase in these slurries. Since the analyses performed were for total metals, as is called for in the protocol, this is not surprising. This also explains why most of the high values for metals were found in slurry streams.

Further breakdowns of these results by type of process, geographical location, and type of mining are shown in Tables 5, 6 and 7. The upshot of these tabulations is that the single most important difference is whether the coal comes from an acid or alkaline region. The greater frequency of priority metals and the higher concentrations in Northern Appalachia is because this is an acid area.

Organic Compounds in Preparation Plant Waters

The organic priority pollutants found in waters from preparation plants and associated areas are shown in Table 8. Fourteen compounds on the priority pollutant list were found above detectable limits. Some of these were found frequently and some only once.

These results should be viewed skeptically since the coal mining industry was the first industry to be screened for the priority pollutants. Many lessons were learned in the process, and these are being applied to the treatability studies and the verification sampling underway at present. They have been a most useful guide.

The prevalence of organic pollutants was examined from the standpoint of industry characteristics. These were: type of mine drainage (acid or alkaline), type of mining (surface or deep), type of process (water only, heavy media and flotation), and geographical location (Central, Northern Appalachia, Southern Appalachia). The data base was not sufficient to categorize the industry by coal seam or coal rank.

No clear pattern was discernible in these classifications except, perhaps, that preparation plants and associated areas in the Central Region have a more frequent occurrence of organic pollutants.

TABLE 5

COMPARISON OF PREPARATION PLANT WASTEWATERS BY PROCESS TYPE

	HEAVY MEDIA AND FROTH FLOTATION			WATER ONLY		
	Frequency	Range (mg/l)		Frequency	Range (mg/l)	
Metal	(10 Streams)	Low	High	(8 Streams)	Low	High
Antimony	4	0.001	0.003	5	0.001	0.021
Arsenic	7	0.002	1.23	8	0.005	0.17
Beryllium	0	—	—	1	—	0.007
Cadmium	0	—	—	1	—	0.032
Chromium	3	0.024	2.0	7	0.033	0.44
Copper	5	0.004	0.72	6	0.044	0.21
Iron*	10	0.098	210.0	7	0.02	3,000
Lead	1	—	0.76	3	0.06	0.167
Manganese*	10	0.01	20.0	8	0.025	39.0
Mercury	6	0.0001	0.0075	5	0.0001	0.0008
Nickel	2	0.05	0.53	2	0.05	0.921
Selenium	2	0.001	0.41	4	0.003	0.16
Silver	0	—	—	0	—	—
Thallium	3	0.001	0.009	4	0.001	0.070
Zinc	7	0.025	1.0	8	0.031	1.37
Cyanides	0	—	—	0	—	—
Phenols	2	0.02	0.035	0	—	—

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* Not on the priority pollutant list, but one on which the industry is regulated

TABLE 6

COMPARISON OF PREPARATION PLANTS AND ASSOCIATED AREAS BY REGION

Metal	N. Appalachian and Ohio Region			S. Appalachian Region			Central Region		
		Range			Range			Range	
	Frequency (10 Streams)	Low	High	Frequency (8 Streams)	Low	High	Frequency (5 Streams)	Low	High
Antimony	6	0.001	0.028	3	0.001	0.003	5	0.002	0.007
Arsenic	10	0.003	1.34	8	0.002	0.045	5	0.005	0.028
Beryllium	1	-	0.22	0	-	-	1	-	0.007
Cadmium	0	-	-	0	-	-	1	-	0.032
Chromium	6	0.024	0.98	1	-	2.0	3	-	0.115
Copper	9	0.004	1.0	2	0.004	0.006	2	-	0.056
Iron*	10	0.098	9000.	8	0.103	9.0	4	-	7.63
Lead	4	0.06	1.0	0	-	-	1	-	0.167
Manganese*	10	0.025	80.0	7	0.024	2.09	4	-	39.0
Mercury	7	0.001	0.0075	7	0.001	0.0048	4	-	0.0007
Nickel	4	0.05	10.0	1	-	0.53	1	-	0.921
Selenium	8	0.005	0.45	6	0.001	0.004	3	0.003	0.005
Silver	0	-	-	0	-	-	0	-	-
Thallium	5	0.001	0.07	2	0.002	0.003	1	-	0.004
Zinc	9	0.025	30.0	3	0.037	0.168	5	0.029	1.37
Cyanide	0	-	-	0	-	-	0	-	-
Phenols	1	-	0.025	3	0.030	0.035	0	-	-

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* Not on the priority pollutant list, but one on which the industry is regulated

TABLE 7

COMPARISON OF PREPARATION PLANTS BY TYPE OF MINING

Metal	Surface Mines			Deep Mines		
	Frequency (9 Streams)	Range (mg/l) Low	High	Frequency (11 Streams)	Range (mg/l) Low	High
Antimony	7	0.001	0.021	4	0.001	0.008
Arsenic	9	0.002	1.23	11	0.002	0.17
Beryllium	1	—	0.007	1	—	0.02
Cadmium	1	—	0.032	0	—	—
Chromium	6	0.024	2.0	5	0.024	2.0
Copper	6	0.004	0.72	5	0.004	0.27
Iron*	8	0.02	3,000	11	0.098	200
Lead	3	0.06	0.76	1	—	0.067
Manganese*	9	0.046	39.0	10	0.01	6.32
Mercury	7	0.0001	0.0075	6	0.0001	0.0009
Nickel	4	0.05	0.921	2	0.05	0.095
Selenium	3	0.001	0.41	3	0.001	0.16
Silver	0	—	—	0	—	—
Thallium	3	0.001	0.070	4	0.001	0.039
Zinc	8	0.029	1.37	8	0.025	1.0
Cyanides	0	—	—	0	—	—
Phenols	1	—	0.025	1	—	0.035

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* Not on the priority pollutant list, but one on which the industry is regulated

TABLE 8

OCCURRENCE OF ORGANIC PRIORITY POLLUTANTS IN COAL PREPARATION PLANTS AND ASSOCIATED AREAS

Compound	Frequency (21 streams)	Concentration Range (μg/l) Low	Concentration Range (μg/l) High
methylene chloride	21	2.6	66,000
chloroform	17	1.6	476
1,1,1,-trichloroethane	5	1.4	2
trans-dichloroethene	7	1.4	10
tetrachloroethene	7	1.4	20
trichlorofluoromethane	2	14	22
chlorobenzene	1	-	12
2,6-dinitrotoluene	1	-	30
benzene	9	0.3	48
toluene	11	0.3	30
ethylbenzene	1	-	>0.2
anthracene/phenanthrene*	1	-	20
diethyl phthalate	2	110	790
di-n-butyl phthalate	4	210	630
bis(2-ethylhexyl) phthalate	11	10	6,100

* Analytical method (GC/MS) cannot distinguish between these two compounds.

TABLE 9

FREQUENCY & RANGE OF ORGANIC PRIORITY POLLUTANTS IN PREP. PLANTS AND ASSOCIATED AREAS

	FREQUENCY		CONCENTRATION RANGE (μg/l)			
COMPOUND	Prep Plants (14 Streams)	Assoc. Areas (7 Streams)	Prep Plants Low	High	Assoc. Areas Low	High
methylene chloride	14	7	2.6	20,000	348	66,000
chloroform	13	4	1.6	152	19	476
1,1,1-trichloroethane	4	1	1.4	2		1.7
trans-dichloroethene	5	2	1.4	10	1.7	1.0
tetrachloroethene	6	1	1.4	20		1.2
trichlorofluoromethane	1	1		14		22
chlorobenzene		1				12
2,6-dinitrotoluene	1	0		30	-	-
benzene	5	4	0.3	12	6.3	48
toluene	6	5	0.3	5.1	2.0	30
ethylbenzene	1	0		>0.2	-	-
anthracene/phenanthrene*	1	0		20	-	-
diethyl phthalate	2	0	110	790	-	-
di-n-butyl phthalate	3	1	270	630		210
bis(2-ethylhexyl) phthalate	9	2	13	1,200	10	6,100

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*The analytical method (GC/MS) cannot distinguish between these two compounds.

TABLE 10
FREQUENCY OF ORGANICS BY SUBCATEGORY

Compound	TYPE OF MINING		GEOGRAPHICAL REGION			TYPE DRAINAGE	
	Deep (7 Streams)	Surface (7 Streams)	Central (4)	No. Appal. (7)	So. Appal. (3)	Acid (8)	Alka-line (6)
methylene chloride	7	7	4	7	3	8	6
chloroform	7	6	4	6	3	7	6
1,1,1-trichloroethane	3	1	2	1	1	1	3
trans-dichloroethene	4	1	2	2	1	2	3
tetrachloroethene	2	4	3	2	1	3	3
benzene	2	3	3	1	1	2	3
toluene	2	4	3	2	1	3	3
di-ethyl phthalate	2*	0	1	1*	0	1*	1
di-n-butyl phthalate	2*	1	2	0*	1	1*	2
bis(2-ethylhexyl) phthalate	5*	4	4	3*	2	4*	5
Total Number	36	31	28	25	14	32	35
Number per Stream	5.14	4.43	7.00	3.57	4.67	4.00	5.83

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* Only six streams available because of loss of sample in shipment

Treatability Studies

The prevalence of organic priority pollutants in coal mine drainage and preparation plant wastewaters formed the impetus for the treatability studies currently underway at the Environmental Protection Agency's Crown Mine Drainage Control Site near Morgantown, West Virginia. The objectives of this study are to:

1. demonstrate the effectiveness of the treatment currently in use (BPT) for removal of certain organic priority pollutants, and
2. determine the effectiveness of, including costs, additional treatments to further reduce organic pollutant concentrations.

Objective one has been virtually attained, and objective two should be achieved by the end of September. Some preliminary results concerned with the effectiveness of BPT will be presented here.

Without going into the details or the rationale for selecting the compounds to study, the selected priority pollutants are shown in Table 11.

In the studies of acid mine drainage, water was obtained from the mine that had been the source of water for other studies at Crown Field Site. However, this mine had been closed for some six to seven months prior to this study. During that time some changes in composition of the water had occurred, but the water remained acid and ferruginous. On pumping the mine no organic pollutants were found. Consequently the selected pollutants were spiked into the water at the approximate concentrations shown in Table 11.

The spiked acid water was then treated by lime neutralization followed by aeration, flocculation, and settling in that order. The effect of this treatment on the volatiles is shown in Table 12. As can be seen, the removal of volatiles is quite complete. This reduction could be accounted for primarily by the aeration step.

To determine if aeration was causing an air pollution problem or a hazard to personnel in the plant, the air over the aerator (~6 ft. above the water's surface) was monitored using a "Sipin"* pump. Analyses of the

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* Sipin - Anatole J. Sipin Company, 425 Park Avenue, South, New York, New York 10016

TABLE 11

SPIKING CONCENTRATIONS OF SELECTED ORGANIC POLLUTANTS IN ACID MINE DRAINAGE

Compound	Concentration (μg/l)
benzene	56
toluene	35
methylene chloride	250
chloroform	250
trans-dichloroethene	10
1,1,1-trichloroethane	10
tetrachloroethene	30
bis(2-ethylhexyl) phthalate	10,000
di-n-butyl phthalate	1,400

TABLE 12
EFFECTIVENESS OF VOLATILE ORGANIC REMOVAL

Stream Parameter	Spiked Feed (mg)	Average Effluent (mg)	Percent Removal
methylene chloride	87.24	9.15	89.6
trans-dichloroethene	3.48	0.23	93.4
chloroform	87.24	8.06	90.8
1,1,1-trichloroethane	3.48	0.21	94.0
benzene	19.53	1.17	94.0
tetrachloroethene	10.48	0.53	94.9
toluene	12.23	0.75	93.9

Basis: 100 gal feed, 9.45 gal sludge, 90.55 gal effluent samples thus obtained revealed very little in the way of pollutants in the air, as is seen in Table 13. At no time did any concentration even approach the eight hour TLV.

The effect of BPT on the two phthalate esters has not been assessed as yet. A complication developed in reducing the data when a discrepancy in solubilities became evident, i.e., the solubilities found in OHMTADS for these compounds are three orders of magnitude too high.

In addition to acid drainage, alkaline drainage is under study too. The source of water for this is a creek that runs through Crown Field Site, Indian Creek. This creek has a pH of about 7.5 to 7.8, and the total suspended solids varies from about 10 mg/l to 300 mg/l depending on rainfall. This water is pumped to the plant and spiked with the organics. However, in the light of the new solubility data, the composition was changed so that the phthalate concentrations were reduced to 450 µg/l each.

This alkaline water received BPT treatment consisting of settling in the clarifier. In addition, several runs were made where the spiked creek water received aeration before going to the clarifier.

Preliminary work-ups of the data show that aeration was as effective at removing volatiles as in the case of acid water. The results so far on settling only in a clarifier indicate that about 65 to 75 percent of the volatiles are removed.

Analyses of the phthalates are not complete enough at this time to assess any effect of BPT.

At this writing, experiments are going on with reduction of priority metals in alkaline water, on ozonation to remove organics, and on carbon adsorption to remove organics. Once these studies are completed, a more exhaustive discussion of the treatability of coal mine drainage and preparation plant wastewater will be published. Furthermore, this will have the back-up of the verification phase of the sampling study. At that stage an assessment of loads to the environment can be made with some certainty, and the economic impact of any treatment can be determined.

TABLE 13

AIR SAMPLES (Sipin Pump)

Average Daily Organic Concentrations (PPM) Period 5/23 - 6/5/78

Sample Location	1,2-trans dichloro-ethene	chloroform	1,1,1-trichloro-ethane	benzene	tetra-chloro-ethylene	toluene
Plant Aerator	ND	0.126	0.007	0.021	0.031	0.073
Plant Clarifier	ND	0.016	0.021	0.013	0.066	0.053
Chemistry Laboratory (Jim Kennedy)	ND	0.021	0.010	0.024	0.038	0.018
Office - Receptionist Desk	0.071	0.024	0.012	0.009	0.054	0.045
Control - Bathroom in Back Office	0.067	ND	0.009	0.010	0.023	0.021
Threshold Limit[1] Values Time-Weighted Average (8-hour workday)	200	25	10	1.0	100	100

[1] These TLV's represent the time-weighted average concentration for a normal 8-hour workday or 40-hour workweek, to which normally all workers may be repeatedly exposed, day after day, without adverse effect.

ND = Not Detectable

APPENDIX A

LIST OF PRIORITY POLLUTANTS

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Priority Pollutants

acenapthene
acrolein
acrylonitrile
benzene
benzidene
carbon tetrachloride (tetrachloromethane)
chlorobenzene
1,2,4-trichlorobenzene
hexachlorobenzene
1,2-dichloroethane
1,1,1-trichloroethane
hexachloroethane
1,1-dichloroethane
1,1,2-trichloroethane
1,1,2,2-tetrachloroethane
chloroethane
bis(chloromethyl)ether
bis(2-chloroethyl) ether
2-chloroethyl vinyl ether (mixed)
2-chloronapthalene
2,4,6-trichlorophenol
parachlorometa cresol
chloroform (trichloromethane)
2-chlorophenol
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
3,3'-dichlorobenzidine
1,1-dichloroethylene
2,4-dichlorophenol
1,2-dichloropropane
1,2-dichloropropylene (1,3-dichloropropene)
2,4-dimethylphenol
2,4-dinitrotoluene
2,6-dinitrotoluene
1,3-diphenylhydrazine
ethylbenzene
fluoranthene
4-chlorophenyl phenyl ether
4-bromophenyl phenyl ether
bis(2-chloroisopropyl) ether
bis(2-chloroethoxy) methane
methylene chloride (dichloromethane)
methyl chloride (chloromethane)
methyl bromide (bromomethane)
bromoform (tribromomethane)
dichlorobromomethane
trichlorofluoromethane
dichlorodifluoromethane
chlorodibromomethane
hexachlorobutadiene
hexachlorocyclopentadiene
isophorone
napthalene
nitrobenzene
2-nitrophenol
4-nitrophenol
2,4-dinitrophenol
4,6-dinitro-o-cresol
N-nitrosodimethylamine
N-nitrosodiphenylamine
N-nitrosodi-n-propylamine
pentachlorophenol
phenol
bis(2-ethylhexyl) phthalate
butyl benzyl phthalate
di-n-butyl phthalate
di-n-octyl phthalate
diethyl phthalate
dimethyl phthalate
benzo(a)anthracene (1,2-benzanthracene)
benzo(a)pyrene(3,4-benzopyrene)
3,4-benzofluoranthene
benzo(k)fluoranthene (11,12-benzofluoranthene)
chrysene
acenaphthylene

anthracene
benzo(ghi)perylene(1,12-benzoperylene)
fluorene
phenanthrene
dibenzo(a,h)anthracene (1,2,5,6-dibenzanthracene)
indeno(1,2,3-cd) pyrene (2,3-o-phenylenepyrene)
pyrene
tetrachloroethylene
toluene
trichloroethylene
vinyl chloride (chloroethylene)
aldrin
dieldrin
chlordane
$4,4^{1}$-DDT
$4,4^{1}$-DDE(p,p^{1}-DDX)
$4,4^{1}$-DDD(p,p^{1}-TDE)
a-endosulfan-Alpha
b-endosulfan-Beta
endosulfan sulfate
endrin
endrin aldehyde
heptachlor
heptachlor epoxide
a-BHC-Alpha
b-BHC-Beta
r-BHC-(lindane)-Gamma
g-BHC-Delta
PCB-1242 (Arochlor 1242)
PCB-1254 (Arochlor 1254)
PCB-1221 (Arochlor 1221)
PCB-1232 (Arochlor 1232)
PCB-1248 (Arochlor 1248)
PCB-1260 (Arochlor 1260)
PCB-1016 (Arochlor 1016)
toxaphene
antimony (total)
arsenic (total)
asbestos (fibrous)
beryllium (total)
cadmium (total)
chromium (total)
copper (total)
cyanide (total)
lead (total)
mercury (total)
nickel (total)
selenium (total)
silver (total)
thallium (total)
zinc (total)

APPENDIX B
ANALYTICAL RESULTS
CLASSICS AND METALS

PREPARATION PLANTS

CLASSICAL PARAMETERS (mg/l)	Prep Plant Drag Tank Raw Water	Slurry Pond Effluent	Prep. Plant Raw Water	Slurry Pond Effluent	Prep Plant Slurry	Slurry Pond Effluent	Clear Lake Prep Plant Recycle	Prep. Plant Make-up	Prep Plant Thickener
Total Solids	9,600	1,100	38,000	240				6710	19,000
Total Suspended Solids	7,800	7.4	37,000	11.8				14.8	15,000
Total Volatile Solids	3,200	150	28,000	220				570	16,000
Volatile Suspended Solids	2,000	3.6	28,000	2.4				4.0	4,200
COD	4,861	20.6	14,700	27.2				12.1	48,000
TOC	1,130	3.2	1,100	9.2				2.7	8,300
pH	6.78	8.20	4.2	4.4				7.4	6.4
METALS (mg/l)									
Aluminum	300.0	< 0.099	50	1.76	200	<0.099	<0.099	<0.099	60.0
Antimony	0.021	0.001	0.002	<0.001	<0.1	<0.05	<0.05	0.007	0.008
Arsenic	0.065	0.007	1.23	0.004	<0.01	<0.002	<0.002	0.028	0.17
Barium	2.0	0.025	0.66	0.149	7.0	<0.005	<0.005	<0.005	0.32
Beryllium	< 0.02	<0.002	<0.02	<0.002	<0.02	<0.002	<0.002	<0.002	0.02
Boron	< 0.050	0.085	0.16	0.014	2.0	0.570	0.431	0.651	0.05
Cadmium	< 0.20	<0.02	<0.2	<0.02	<0.2	<0.02	<0.02	<0.02	< 0.2
Calcium	268	175	8.0	26.5	947	202	218	250	194
Chromium	0.44	0.036	<0.24	<0.024	<0.24	0.103	0.107	0.041	< 0.24
Cobalt	< 0.10	<0.01	0.12	0.118	<0.1	<0.01	<0.01	<0.01	0.15
Copper	0.21	0.03	0.72	0.044	0.27	<0.004	<0.004	<0.004	0.19
Iron	3000.0	0.183	210	0.803	200	0.200	0.352	0.161	200
Lead	< 0.60	0.067	0.76	<0.06	<0.6	<0.06	<0.06	<0.06	< 0.6
Magnesium	130	55.9	8.0	10.3	287	150	160	100	35.0
Manganese	2.0	0.025	20.0	3.870	2	0.024	0.097	0.046	4.0
Mercury	0.0003	<0.0001	0.0075	0.0016	<0.0005	<0.0005	<0.0005	0.0004	0.0008
Molybdenum	0.55	0.03	0.16	<0.01	0.190	<0.01	<0.01	<0.01	< 0.1
Nickel	< 0.50	< 0.05	<0.5	0.11	<0.5	<0.05	<0.05	<0.05	< 0.5
Selenium	0.059	0.012	0.41	<0.006	0.05	<0.005	<0.005	0.003	0.16
Silver	< 0.25	< 0.025	<0.25	<0.025	<0.025	<0.025	<0.025	<0.025	< 0.25
Sodium	53.0	44.5	13.0	15.1	764	670	513	1200	313
Thallium	0.070	< 0.001	0.009	<0.001	<0.1	<0.1	<0.1	0.004	0.039
Tin	< 0.99	< 0.099	<0.99	<0.099	<0.99	<0.099	<0.099	<0.099	< 0.99
Titanium	2.0	< 0.01	0.12	<0.01	3.0	0.012	<0.01	<0.01	0.52
Vanadium	< 0.99	< 0.099	<0.99	<0.099	<0.99	<0.099	<0.099	<0.099	<0.99
Yttrium	0.12	< 0.01	<0.1	<0.01	<0.1	0.013	0.011	<0.01	< 0.1
Zinc	0.81	0.039	0.48	0.497	1.0	0.049	0.026	0.071	1.0
Cyanide	< 0.005	< 0.005	<0.005	<0.005				<0.005	< 0.005
Phenol			0.025	<0.02					
	NC-22		V7			NC-3		NC-7	NC-21

PREPARATION PLANTS

CLASSICAL PARAMETERS (mg/l)	PREP PLANT RECYCLE POND	Slurry Pond Effluent	Slurry Pond Effluent	Prep.Plant Recycle Pond	Prep. Plant Recycle Pond	Prep.Plant Recycle Pond	Prep. Plant Water Circuit	Slurry Pond Effluent	Slurry Lagoon	Slurry Lagoon
Total Solids	2200	3700	1200	2750	850	680	7,800	530	7.0	2200
Total Suspended Solids	8.0	11.8	5.4	2.2	4.0	50	230	24		11.2
Total Volatile Solids	220	420	100	460	38	100	1,100	94	140	210
Volatile Suspended Solids	1.6	4.8	1.8	<1.0	1.6	5.6	140	22		
COD	11.6	37.1	<2.0	4.0	4.0	23.3	396	31.0	33.3	10.4
TOC	<1.0	16.2	<1.0	<1.0	2.0	<1.0	43.2	25.0	11.6	1.8
pH	6.4	7.0	9.0	2.9	8.1	7.2	7.3	7.1	9.1	7.02
METALS (mg/l)										
Aluminum	<0.099	<0.099	<0.099	10.0	<0.099	<0.99	<0.099	0.747	<0.099	<0.099
Antimony	0.004	0.001	0.002	0.005	0.002	<0.001	0.003	<0.001	0.003	0.001
Arsenic	0.005	0.030	0.014	0.008	0.008	0.002	0.045	0.002	0.003	0.04
Barium	<0.005	0.025	0.035	<0.005	0.025	0.11	0.161	0.068	0.01	<0.005
Beryllium	<0.002	<0.002	<0.002	0.007	<0.002	<0.02	<0.002	<0.002	<0.002	<0.002
Boron	0.271	0.085	0.261	0.072	0.055	0.09	0.007	0.046	131	0.067
Cadmium	<0.02	<0.02	<0.02	0.032	<0.02	<0.2	<0.02	<0.02	<0.02	<0.02
Calcium	336	175	64.1	0.254	55.3	35.0	39.6	13.3	197	313
Chromium	0.033	0.036	<0.024	0.115	<0.024	2.0	<0.024	<0.024	<0.024	0.040
Cobalt	<0.01	<0.10	<0.01	0.356	<0.01	<0.1	<0.01	<0.01	<0.01	0.043
Copper	0.007	0.030	<0.004	0.056	<0.004	<0.04	<0.004	0.005	0.046	<0.004
Iron	<0.02	0.188	0.271	7.63	0.181	9.0	0.195	0.487	0.098	0.227
Lead	<0.06	0.067	<0.06	0.167	<0.06	<0.6	<0.06	<0.06	<0.06	<0.06
Magnesium	54.4	55.9	29.1	0.140	15.8	16.0	8.8	6.4	21.7	69.3
Manganese	0.147	0.025	0.064	39.0	<0.01	0.37	0.024	<0.024	0.108	6.320
Mercury	<0.0001	<0.0001	0.0006	0.0007	0.0004	0.0009	0.002	0.0003	<0.0001	0.0003
Molybdenum	<0.01	0.030	0.041	0.028	0.029	<0.1	<0.01	<0.01	0.021	0.015
Nickel	<0.05	<0.05	<0.05	0.921	<0.05	0.53	<0.05	<0.05	<0.05	0.095
Selenium	0.004	0.019	<0.001	0.005	<0.001	<0.001	0.002	<0.001	0.007	0.006
Silver	<0.025	<0.025	<0.025	<0.025	<0.025	<0.25	<0.025	<0.025	<0.025	<0.025
Sodium	134	44.5	226	43.1	163	67.0	167	97.0	89	143
Thallium	<0.001	0.002	0.001	0.001	<0.001	<0.001	0.002	0.003	0.001	<0.001
Tin	<0.099	<0.099	<0.099	<0.099	<0.099	<0.99	<0.099	<0.099	<0.099	<0.099
Titanium	<0.01	<0.010	0.011	<0.01	0.016	<0.1	<0.01	<0.01	<0.01	<0.01
Vanadium	<0.099	<0.099	<0.099	<0.099	<0.099	<0.99	<0.099	<0.099	<0.099	<0.099
Yttrium	0.013	<0.010	<0.01	0.140	<0.01	<0.1	<0.01	<0.01	<0.01	0.012
Zinc	0.031	0.039	0.029	1.37	0.093	<0.25	<0.025	0.04	<0.025	0.081
Cyanide	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Phenol	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.035	<0.02	<0.02	<0.02
		3.1 x 10^4								
	NC-5	T5	NC-8	NC-9	NC-10	NC-11	NC-16	NC-17	NC-18	NC-19

ASSOCIATED AREAS

CLASSICAL PARAMETERS (mg/l)	Refuse Pile Raw Water	Refuse Pile Treated Effluent	Refuse Pile Raw Water	Refuse Pile Runoff Non-Discharging Pond	Refuse Pile Non-Discharging Pond	Refuse Pile Raw Water	Storage Pile Runoff Untreated
Total Solids	410	260	14,000	490	430	22,000	180
Total Suspended Solids	11.4	62	39	26.4	3.8	140	18.4
Total Volatile Solids	34	36	2,600	86	66	2,900	26
Volatile Suspended Solids	2.2	19.6	6.0	4.8	<1.0	28.0	4.8
COD	15.5	29.1	260	31.0	19.4	1,160	15.5
TOC	3.6	5.5	19.3	2.9	2.4	11.1	<1.0
pH	4.0	9.7	6.5	7.7	7.2	2.4	7.2
METALS (mg/l)							
Aluminum	1.47	<0.99	5.0	<0.099	<0.099	800	<0.099
Antimony	0.002	0.002	0.008	<0.001	<0.001	0.028	<0.001
Arsenic	0.003	0.004	0.055	0.007	0.004	1.34	0.002
Barium	0.127	0.17	<0.05	0.649	0.009	< 0.05	<0.005
Beryllium	<0.002	<0.02	<0.02	<0.002	<0.002	0.22	<0.002
Boron	0.024	0.11	1.000	<0.005	0.028	< 0.05	<0.005
Cadmium	<0.02	<0.2	<0.2	<0.02	<0.02	< 0.20	<0.02
Calcium	26.5	8.0	485	14.5	17.5	407	4.7
Chromium	<0.024	<0.24	0.43	<0.024	<0.024	0.98	<0.024
Cobalt	0.038	<0.1	<0.1	<0.01	<0.01	4.0	<0.01
Copper	0.006	<0.04	0.31	<0.004	<0.004	1.0	<0.004
Iron	0.509	1.0	2,000	0.123	0.103	9,000	0.275
Lead	<0.06	<0.6	<0.6	<0.06	<0.06	1.0	<0.06
Magnesium	15.5	3.0	420	3.7	11.1	490	0.8
Manganese	2.09	<0.2	30	0.029	0.600	80.0	0.027
Mercury	0.0048	0.0043	0.0002	0.0003	0.0001	0.0011	0.0007
Molybdenum	<0.01	<0.1	0.39	<0.01	0.112	2.0	<0.01
Nickel	<0.05	<0.5	1.0	<0.05	<0.05	10.0	<0.05
Selenium	0.003	0.004	0.074	0.003	0.002	0.45	0.001
Silver	<0.025	<0.250	<0.25	<0.025	<0.025	< 0.25	<0.025
Sodium	38.8	65.0	913	55.4	139	413	0.7
Thallium	<0.001	<0.001	<0.001	<0.001	<0.001	0.014	<0.001
Tin	<0.099	<0.99	<0.99	<0.099	<0.099	1.0	<0.099
Titanium	0.014	<0.1	<0.1	<0.01	<0.01	< 1.0	<0.01
Vanadium	<0.099	<0.99	<0.99	<0.099	<0.099	< 0.99	<0.099
Yttrium	<0.01	<0.1	0.31	<0.01	<0.01	3.0	<0.01
Zinc	0.168	<0.25	0.99	<0.025	0.037	30.0	<0.025
Cyanide	<0.005	<0.005	<0.005	<0.005	<0.005	< 0.005	<0.005
Phenols	<0.02	0.035	<0.02	0.03	<0.02	<0.02	<0.02
Asbestos (fibers/l)							
	NC-15		NC-14	NC-16	NC-17	NC-21	NC-12

APPENDIX C

ANALYTICAL RESULTS

ORGANICS

PREPARATION PLANTS

Priority Pollutants, µg/l	DRAG TANK RAW WATER	SLURRY POND EFFLUENT	Prep Plant Slurry	Settling Pond Effluent	Prep Plant Slurry*	Slurry Pond Effluent*	Clear Lake Prep Plant Recycle*
benzene	ND	ND	ND	ND			
chlorobenzene	ND	ND	ND	ND			
1,2-dichloroethane	ND	ND	ND	ND			
1,1,1-trichloroethane	ND	ND	ND	ND			
1,1,2,2-tetrachloroethene	ND	ND	ND	>11			
chloroform (trichloromethane)	10	ND	29	>10			
1,2-trans-dichloroethylene	ND	ND	ND	ND			
2,6-dinitrotoluene	30	ND	ND	ND			
ethylbenzene	ND	ND	ND	>0.2			
methylene chloride	930	1800	199	1,700			
trichlorofluoromethane	ND	ND	ND	ND			
toluene	ND	ND	ND	>4.2			
bis(2-ethylhexyl) phthalate	ND	ND	ND	330			
di-n-butyl phthalate	ND	ND	ND	ND			
diethyl phthalate	ND	ND	ND	ND			
anthracene	20*	ND	ND	ND			
phenanthrene	20*	ND	ND	ND			

NC-22 V7 NC-3

*Method does not distinguish between these compounds

PREPARATION PLANTS

Priority Pollutants, µg/l	Prep Plant Recycle Pond	Slurry Pond Effluent	Slurry Pond Effluent	Acid Prep Plant Recycle Pond	Prep Plant Recycle Pond	Prep Plant Recycle Pond	Prep Plant Water Circuit	Slurry Pond Effluent	SLURRY LAGOON	SLURRY LAGOON
benzene	0.3	0.7	12	6.2	ND	ND	ND	1.2	ND	ND
chlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-trichloroethane	ND	2.0	1.6	ND	1.4	ND	ND	1.8	ND	ND
1,1,2,2-tetrachloroethene	1.4	13.6	5.2	4.5	ND	ND	ND	20	ND	ND
chloroform (trichloromethane)	5.0	18	18	7.3	12.	152	1.6	21	78	20
1,2-trans-dichloroethylene	ND	1.9	1.4	ND	1.5	ND	ND	2.6	10	ND
2,6-dinitrotoluene	ND	ND	ND	ND	ND	ND	ND	ND		ND
ethylbenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
methylene chloride	2.6	20,000	>2,300	>4,200	14,000	1,500	7,100	20,000	1220	450
trichlorofluoromethane	ND	14	ND	ND	ND	ND	ND	ND	ND	ND
toluene	0.3	0.3	5.1	1.8	ND	ND	ND	0.3	ND	ND
bis(2-ethylhexyl) phthalate	200	860	420	280	380	ND	1,200	510		13
di-n-butyl phthalate	ND	ND	ND	630	560	ND	ND	270		ND
diethyl phthalate	ND	ND	790	ND	110	ND	ND	ND		ND
anthracene	ND	ND	ND	ND	ND	ND	ND	ND		ND
phenanthrene	ND	ND	ND	ND	ND	ND	ND	ND		ND
	NC-5	NC-8	T-5	NC-9	NC-10	NC-11	NC-16	NC-17	NC-18	NC-19

ASSOCIATED AREAS

Priority Pollutants, µg/l	Refuse Pile Raw Water	Refuse Treated Effluent	Refuse Pile Raw Water	Refuse Pile Runoff Non-Discharging Pond	Refuse Pile Non-Discharging Pond	REFUSE PILE RAW WATER	Storage Pile Runoff Untreated
benzene	48	6.3	44	ND	10	ND	ND
chlorobenzene	ND	ND	12	ND	ND	ND	ND
1,2-dichloroethane	ND	ND	ND	ND	ND	ND	ND
1,1,1-trichloroethane	ND	1.7	ND	ND	ND	ND	ND
1,1,2,2-tetrachloroethene	ND	1.2	ND	ND	ND	ND	ND
chloroform (trichloromethane)	45	19	ND	26	ND	ND	476
1,2-trans-dichloroethylene	ND	1.7	ND	ND	10	ND	ND
2,6-dinitrotoluene	ND	ND	ND	ND	ND	ND	ND
ethylbenzene	ND	ND	ND	ND	ND	ND	ND
methylene chloride	480	66,000	1,440	654	967	348	1,100
trichlorofluoromethane	ND	22	ND	ND	ND	ND	ND
toluene	14	2.0	27	ND	30	10	ND
bis(2-ethylhexyl) phthalate	ND	6,100	ND	ND	ND	ND	10
di-n-butyl phthalate	ND	210	ND	ND	ND	ND	ND
diethyl phthalate	ND	ND	ND	ND	ND	ND	ND
anthracene	ND	ND	ND	ND	ND	ND	ND
phenanthrene	ND	ND	ND	ND	ND	ND	ND
	NC-15		NC-14	NC-16	NC-17	NC-21	NC-12

CONTROL OF TRACE ELEMENT LEACHING FROM COAL PREPARATION WASTES

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ABSTRACT

The aqueous drainage from coal refuse dumps often is contaminated with acids and a variety of potentially toxic trace and inorganic constituents. The Los Alamos Scientific Laboratory is involved in a research program, which is jointly supported by EPA and DOE, to identify suitable methods to control or abate this form of environmental pollution. Control methods that are currently under investigation include techniques to immobilize or remove the contaminating substances from coal cleaning wastes prior to disposal, treatment of refuse dumps to prevent the release of pollutants from them, and treatment of contaminated waters as they emerge from refuse disposal sites. The emphasis of this paper is to review experimental results that have been obtained in this program to date, and to discuss the various environmental control options available to the coal cleaning industry.

INTRODUCTION

The mineral wastes from coal preparation and mine development constitute a major environmental problem. Over 3-billion tons of these materials have accumulated in the U.S., and the current annual rate of waste production of 100-million tons per year is expected to double within a decade (National Academy of Sciences, 1975). The total number of coal waste dumps is estimated to be between 3000 and 5000 of which one-half pose some type of health, environmental or safety problem (National Academy of Sciences, 1975). Structural weaknesses in coal refuse banks have led to tragic landslides such as those at Buffalo Creek, WV and Aberfan, Wales, and the 300 or so burning waste banks are a major source of air pollution. In addition to these problems, there is growing concern about environmental effects from the trace elements that are present in the highly mineralized, acid drainage from coal refuse dumps that affects many thousands of miles of streams and waterways.

Although it has been established that the drainage from coal refuse dumps is often highly contaminated with trace or inorganic elements, little is known about the quantities of undesirable elements that are released into the environment from this source (Wewerka, et al., 1976). Development of the necessary control technologies for human and environmental protection requires quantitative evaluation of the extent and severity of the problem. LASL has been directed by DOE and EPA to assess the nature and magnitude of the trace elements in the drainage from coal preparation wastes, to identify the trace elements of greatest environmental concern in these materials, and to evaluate required pollution control technology for this form of environmental contamination.

This program is divided into several research activities. The initial efforts included studies of the structure and weathering and leaching behaviors of the trace elements in selected samples of high sulfur refuse and coal (Wewerka, et al., 1978a and b). These investigations established the overall potential of these materials to cause trace element contamination, and revealed the identities of the specific trace elements of concern in the refuse and coal pile effluents. The information gathered on refuse and coal structure and environmental behavior provided the basis for the present stage of the program, which involves assessment or development of control technology to lessen the environmental impact of trace element pollution of coal or refuse associated waters.

Investigations are now underway to identify the options for preventing or controlling trace element contamination of the drainages from high sulfur coal preparation wastes. Two basic approaches to effect trace element control are being considered in this work. The first involves methods to treat newly produced coal refuse either at the preparation plant or during disposal to prevent the eventual release of trace elements from the disposal site. These techniques include refuse calcining, treatment of the refuse to remove acid forming constituents and labile trace elements, and the application of adsorbents or attenuating agents to refuse disposal sites. The second approach concerns techniques to reduce or abate the trace-element composition of already contaminated waters emerging from refuse dumps or disposal areas. Under consideration here are such methods as alkaline neutralization, ion exchange, reverse osmosis, chelation and application of selected adsorbents. Some of the experimental results from these researches are reviewed and discussed in the following sections of this paper.

EXPERIMENTAL

The coal preparation wastes used in this work were collected from three coal cleaning plants (designated Plants A, B and C) in the Illinois Basin. These samples of high sulfur coal refuse are typical of the wastes produced by cleaning of the major coal types currently mined in the region (Wewerka, et al., 1978a).

The mineral and elemental compositions of the raw refuse samples, calcined refuse materials and mixtures of refuse with other materials were analyzed by x-ray diffraction, neutron activation analysis, atomic absorption spectrophotometry, optical emission spectroscopy and wet chemical methods.

Both static and dynamic leaching experiments were conducted to evaluate the behavior of the trace elements in the Illinois Basin coal wastes under simulated environmental conditions and to test the effectiveness of potential environmental control methods. The static experiments were carried out by agitating a known quantity of crushed refuse or composite (50 g) in the presence of a constant volume of distilled water (250 ml) for varying periods of time. In the dynamic or column leaching tests, a crushed sample (~ 1500 g) was packed into a 70-cm-long by 4.6 cm-diam glass column and distilled water was continuously monitored through the column at a rate of 0.5 ml/min. The elemental compositions of the experimental leachates were determined by the techniques mentioned above.

The details of the experimental set ups and analytical procedures used in this study appear in two recently published reports (Wewerka, et al., 1978a and b).

RESULTS AND DISCUSSION

The Illinois Basin coal refuse samples used in this study were composed of clay minerals (illite, kaolinite and other more complex clays), quartz, pyrite, and marcasite. Interspersed throughout the mineral network were a variety of minor minerals and residual coal. The relative magnitudes of the major minerals constituting these refuse materials did not vary greatly from sample to sample.

Elementally, these refuse materials were found to be very complex. Some 55 elements were identified in most of the refuse samples and undoubtedly there are more (Wewerka, et al., 1978b). The most abundant of these elements, Fe, Al and Si, comprise the structures of the major mineral systems. The minor elements are present as constituents of minor minerals, components of the residual coal or substituents in the major mineral lattices.

Static and dynamic leaching experiments were performed to evaluate the trace element behavior of Illinois Basin coal wastes under simulated weathering conditions. These experiments were done to provide information needed to predict quantitatively the trace element levels in the drainage from coal refuse dumps or disposal areas and to identify those elements of environmental concern.

Perhaps the single most important characteristic of the high sulfur refuse materials during aqueous leaching is their pronounced tendency to rapidly produce acidic leachates. This is due to the oxidative degradation of the pyrite and marcasite present in the refuse. Acid formation is partially attenuated by calcite or other neutralizing species in the refuse, but the leachates from the Illinois Basin refuse samples that we studied nearly always had pH values in the range of 2 to 4. These acid leachates are very efficient in dissolving or degrading many of the mineral components of the refuse, and thus releasing the trace or minor elements associated with them. Figure 1 depicts the relationship between leachate pH and the dissolved solids contents of the leachates in contact with the various refuse samples.

Two types of trace element leachabilities were observed for all of the Illinois Basin refuse samples. Because of their abundances in the refuse some elements (such as Fe, Al, Ca, Mg) are released in relatively high absolute quantities (Table 1). Other, less abundant elements (for example, Ni, Co, Zn, Cu) are leached in a high proportion to the total of each present, although this may not be a large amount in the absolute sense (Table 2). The first group is highly concentrated in the leachates, the second is highly leachable from the refuse. A similar trace element release behavior was also observed during the dynamic leaching of these refuse materials.

Multimedia Environmental Goals (MEGs) were used to identify the hazardous trace elements in the leachates from the refuse materials studied (Cleland and Kingsbury, 1977). MEGs are defined as levels of potentially hazardous effluents that are appropriate for preventing negative effects in exposed ecosystems or represent control limits achievable through current technology.

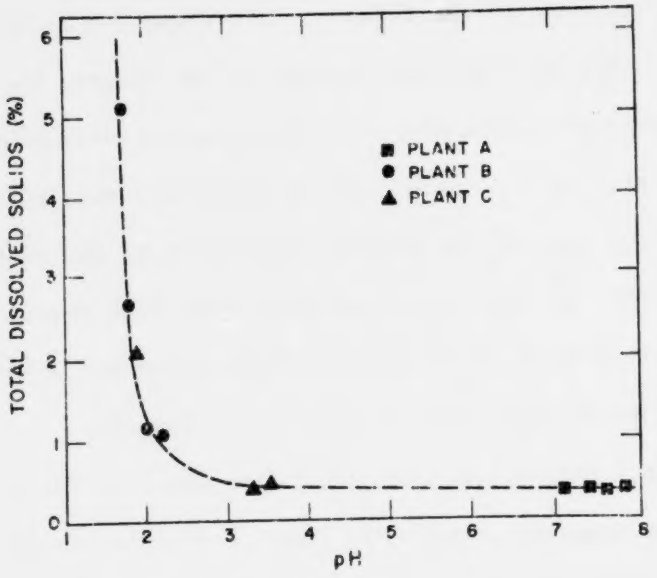

Figure 1. The relationship between pH and total dissolved solids for leachates from static leaching experiments with Illinois Basin coal refuse.

Element	Leachate concentration μg/mℓ	Element	Leachate concentration μg/mℓ
Fe	16400	Co	18
Ca	680	As	7
Al	570	Cu	3.7
Mg	216	Ti	< 2
K	90	V	< 2
Na	74	Cr	1.1
Zn	48	Be	0.2
Mn	40	Cd	0.2
Ni	31	Pb	< 0.2

Table 1. Trace elements released from Illinois Basin coal refuse during static leaching. Results from experiment with Plant B refuse. Conditions: 50 g of -20 mesh refuse agitated with 250 mℓ water, 1 day, room temperature, open vessel.

Element	Percent of total leached	Element	Percent of total leached
Ca	79	Cu	7
Co	60	Be	6
Ni	46	Na	5
Zn	42	V	< 2.5
Cd	35	Cr	1.2
Mn	28	Al	1.2
Fe	14	Pb	< 1.2
As	9	K	0.8
Mg	9	Ti	< 0.1

Table 2. Percent of trace elements released from Illinois Basin Plant B coal refuse during static leaching. Conditions: 50 g of -20 mesh refuse agitated with 250 mℓ water, 1 day, room temperature, open vessel.

The utility of the MEG system is that it provides a means for directly determining which of the contaminants in waste water solutions, such as those of interest here, exceed concentrations that are safely assimulated by the environment. Application of the MEG routine to data on the composition of refuse leachates obtained in this work, and from available information in the literature, has revealed that nine elements, Fe, Al, Mn, Co, Ni, Zn, As and Cd are frequently present in potentially hazardous amounts. Although these elements are not necessarily the only ones in the refuse leachates that could conceivably be troublesome under all circumstances, they are, however, the priority elements that are receiving the greatest emphasis in the current work on environmental control technology.

Research has now been started to identify suitable means to control trace element contamination of the drainages from high sulfur coal preparation wastes. These control techniques can roughly be divided into three categories: (1) immobilization or removal of contaminants prior to disposal of the refuse materials; (2) waste dump treatment to prevent the release of undesirable substance from it; and (3) treatment of already contaminated water discharged from existing refuse disposal sites.* Encouraging results have been obtained from current research on each of these three types of environmental control techniques.

One of the more promising techniques under consideration to immobilize the hazardous elements in high sulfur coal refuse materials is calcining of the refuse to high temperatures to produce an inert glass-like slag. Present work in this area is directed both at identifying the chemical and physical changes brought about in the refuse structure as a result of the heat treatment, and at defining the consequent decreases in trace element mobilities.

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* These studies are directed at environmental control of both surface and groundwater contamination that may result from the disposal of coal preparation wastes either on or near the surface or the deep burial of them in strip or underground mines.

Several calcining experiments have been performed to determine the optimum heat treatment conditions necessary to chemically immobilize the potentially toxic trace elements in the refuse matrix. These experiments were performed using high sulfur coal preparation wastes from Plants B and C (Illinois Basin). The wastes were ground to -20 mesh and calcined in air at 600, 800, 1000, and 1200°C for a 2 h period. The success of the calcining treatment at reducing the trace element mobilities of the refuse samples is illustrated by the data from a comparison leaching experiment incorporating the refuse sample that had been calcined at 1000°C (Table 3). The calcined and uncalcined refuse samples listed in the table had been subjected to static leaching for 48 h. It is seen from the information in the table that calcining has essentially eliminated the acid generating potential of the refuse samples and that the TDS contents of the resulting leachates was substantially reduced. More important is the fact that the concentrations of the abreviated group of toxic elements listed have been reduced in the calcined refuse leachates by about two orders of magnitude over the concentrations in the leachates produced from the raw refuse materials.

Physically, the samples calcined at 1000 and 1200°C began to sinter. X-ray diffraction analyses of the calcined materials suggests that at these temperatures considerable breakdown of the clay mineral structures has begun to occur. This apparently results in significant encapsulation of the leachable refuse components. The acid forming constituents of the refuse samples (pyrite and marcasite) are transformed at lower temperatures to volatile sulfur compounds. This is evidenced by the reduction of the sulfur content of the Plant B refuse material from 13.4 wt % to 0.7 wt % after

	Uncalcined Refuse	Calcined Refuse
pH	2.9	8.0
TDS(%)	0.6	0.2
Al	40	0.3
Fe	240	< 0.02
Mn	2.3	0.02
Co	1.1	0.01
Ni	1.9	0.01
Zn	1.1	0.05

Table 3. Trace element leachability of a coal refuse sample calcined at 1000°C for 2 h. Elemental compositions of leachates are reported as ppm.

calcining to 800°C. This undoubtedly accounts for the marked reduction of the acid generating potential of the calcined refuse samples.

In addition to the research just described on refuse clacining, studies are also being conducted on the effectiveness of preleaching the refuse materials to remove both the acid forming constituents and the mobile trace elements prior to disposal. This work involves the application of water in conjunction with a variety of oxidizing agents to effect contaminant removal.

Several methods are being considered to treat coal refuse during disposal to prevent the release of trace contaminants during subsequent waste dump weathering or leaching by surface or ground water. These include codisposal of the refuse material with neutralizing agents or trace element adsorbents and the application of water tight sealants to all or parts of the waste dump mass.

Especially promising among these techniques is the codisposal of the acid refuse materials with alkaline agents such as lime. In one set of experiments, for example, powdered lime in varying amounts (3 to 50 g) was slurried in 150 ml of distilled water with -3/8 in. high sulfur coal refuse (530 g, from Illinois Basin Plant B). The resultant mixture was subsequently filtered, dried in air at 50°C, and repulverized to -3/8 in. particles. Four different lime concentrations were employed; 0.5, 1.5, 3 and 10 wt %. In addition, a control refuse sample that had not been lime treated was also incorporated into this study for comparison purposes.

Column leaching experiments were conducted with about 500 g of each of the above samples to determine the effects of the lime additions. The refuse mixtures were packed into pyrex columns 25 cm long by 5 cm diameter and subsequently leached with distilled water at a flow rate of 0.5 ml/min until more than 4 ℓ of water had been passed through the refuse beds. The composition of the leachates after about 300 ml of water had passed through the columns containing the refuse mixed with 3 and 10 wt % lime and also through a control column containing untreated refuse are given in Table 4.

Although the data are not listed in Table 4, the leaching experiments showed that the addition of 0.5 and 1.5 wt % lime to the acid refuse had only a small influence on leachate pH and trace element concentration because the acid neutralization provided by these amounts of lime was overwhelmed by the acid generating capability of the refuse. The additions of 3 and 10 wt % of lime, on the other hand (Table 4), did indeed effectively counteract the acid properties of the refuse; the pH of the leachates for these two systems are elevated to acceptable levels and the trace element compositions of the leachates from the treated refuse samples are significantly reduced in all instances.

The system containing 3 wt % lime is especially interesting because a leachate pH of 7 was maintained for nearly the entire duration of the leaching experiment (until 4.2 ℓ had been passed through the column). TDS values for this refuse-lime combination were also very respectable (ranging downward from about 0.6 wt %) especially considering that the dissolution of the lime itself adds substantially to the dissolved solids content of the solution.

As a result of experiments like these, the addition of alkaline agents to refuse disposal sites is viewed to be a very promising means to control acid generation and trace element releases from high sulfur coal refuse, and the research effort in this area is being continued.

Another potentially fruitful way to retain the leachable contaminants within a refuse disposal site is to intermix the acid coal wastes with suitable amounts of trace element attenuating agents. An example of one of the

	Untreated refuse Control	Refuse + 3% Lime	Refuse + 10% Lime
pH	2	7	12
TDS(%)	4	0.4	0.5
Al	720	< 0.6	< 0.5
Fe	7800	40	< 0.1
Mn	22	1	< 0.02
Co	12	0.3	0.1
Ni	18	0.5	0.1
Zn	29	0.1	0.02

Table 4. A few results from a column leaching study of Illinois Basin coal refuse that had been lime treated. Elemental compositions of leachates are given as ppm. Leachate volume 300 mℓ.

preliminary studies conducted in this area will illustrate the potential utility of the method.

In this experiment, acidic coal refuse leachates were equilibrated with several solid sorbent materials to evaluate their trace element attenuation capabilities, prior to using these agents in codisposal experiments. The solids used were illite, montmorillonite, and kaolinite clays; a sample of scrubber sludge, precipitator ash and two samples of bottom ash, each from different power plants; an acid drainage treatment sludge; and a clay rich soil. The experimental procedure consisted of shaking the solid (50 g) with the coal refuse leachate (150 ml) for 15 h, measuring the resulting pH and analyzing the filtrate for trace elements.

Several of these agents proved to be quite effective in attenuating the acid and trace element contents of the refuse leachates. Among these were the fly ash, scrubber sludge and AMD sludge and the illite and montmorillonite clays (Table 5). (An important point to distinguish here is that the fly ash and sludges are themselves alkaline agents, so the effectiveness of these two materials may at least in part be due to pH control of the solutions rather than direct trace element adsorption.) The bottom ash samples, not unexpectedly proved to be too chemically intractable to interact with the contaminated leachates and the one soil studied did not exhibit sufficient exchange capacity to be of use. Other experiments are being conducted, however, to test the trace element and acid absorbtivities of a wide variety a calcareous and noncalcareous soils, and weathered and nonweathered soils from the Illinois Basin.

Studies are also underway to evaluate several techniques for treating refuse drainage water that is contaminated with acids and toxic trace elements.

	Untreated leachate Control	Scrubber Sludge	Fly Ash	Illite
pH	2.6	7.3	9.6	9.1
Al	10	< 0.2	0.6	0.6
Fe	107	< 0.1	0.2	0.3
Mn	4	2.2	0.04	0.3
Co	1.9	0.7	0.1	0.1
Ni	2.6	0.8	< 0.05	0.07
Zn	1.0	0.6	0.02	0.35

Table 5. The attenuation of contaminated coal refuse leachates by various agents. Elemental concentrations in leachates reported as ppm.

Included among these are alkaline neutralization, ion exchange, reverse osmosis, chelation and biological treatment.

These techniques have proven fruitful in attenuating contaminants in many types of industrial or mining waste waters, and may be effective in treating coal refuse drainage.

One of the most promising of these control techniques, alkaline neutralization, is currently used extensively to treat acid drainage from coal mines. While it is well known that alkaline neutralization is very effective in controlling the acid and overall salt compositions of mine waste waters, the degree of control that this method exerts over some of the more highly leachable toxic trace elements remains to be established (Wewerka, et al., 1976). Elaboration of this latter point is the basis for one of the studies now being conducted in this area.

In this work, the degree to which the solubilities of the various trace elements in the drainage from high sulfur coal refuse are effected by neutralization with such agents as limestone and lime is being investigated. The experiments are basically titrations in which limestone, lime or lye (the standard base) were added to one liter of contamined refuse drainage until a predetermined value of the pH was reached. The solutions (or slurries) were allowed to sit overnight, filtered, and the pH, dissolved solids and trace element contents of them were measured. The results of these experiments are summarized in Table 6.

Examination of Table 6 shows that neutralization is an effective technique for decreasing trace element concentrations in refuse waste water. The pH and Fe contents of the treated solutions are within acceptable limits, based on the 1977 EPA effluent limitation guidelines for coal preparation plants (Fe ≤ 3.5 μg/ml averaged for 30 days, pH 6-9). Mn, however, exceeds

	Untreated Leachate Control	Lye	Limestone	Lime
pH	1.1	6	7.1	6.6
TDS(%)	0.5	3.4	3.2	3.2
Al	18	< 0.2	< 0.2	< 0.2
Fe	820	0.06	0.3	0.3
Mn	3.6	0.07	6.4	1.0
Co	2.0	0.05	1.0	0.6
Ni	3.2	0.05	1.0	0.7
Zn	3.9	0.02	0.1	0.1

Table 6. Alkaline neutralization of contaminated refuse drainage. Drainage compositions reported as ppm.

the acceptable level of 2.5-3 μg/ml (averaged for 30 days) in the limestone case. Further work in the area of alkaline neutralization of refuse drainage involves its application to more highly contaminated drainage to investigate coprecipitation phenomenon, and the scale up of the process to more life-like circumstances.

SUMMARY

The purpose of this paper was to present an overview of research underway at Los Alamos Scientific Laboratory to identify the various options for controlling trace element contamination of coal refuse drainages. The control methods under consideration include chemical and physical methods to immobilize or remove undesirable contaminants prior to refuse disposal, the treatment of refuse disposal sites with attenuating agents or sealants to prevent the discharge of contaminated water, and the direct treatment of refuse drainage as it emerges from the refuse disposal site. The initial results from these studies suggest that many of the techniques being considered are technically feasible for controlling trace element contamination of refuse dump drainage.

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STABILIZATION OF COAL PREPARATION PLANT SLUDGES

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ABSTRACT

As operating costs continue to increase, coal producers search for new processes to reduce costs. One major area for improvement is fine coal refuse handling and disposal. Current disposal practices for this material utilize large permanent settling ponds, temporary settling ponds, large permanent impoundments, or mechanically dewatered solids for landfill disposal. This discussion will briefly review Calcilox* additive stabilization techniques, present the latest technical developments, and illustrate Calcilox additive disposal alternatives that can technically and economically improve fine coal refuse disposal.

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* Calcilox (trademark) additive is a registered trademark of Dravo Corporation.

Introduction

Today, the major energy reserve in the United States is coal, which accounts for nearly 80% of the known recoverable resources. Reasonably priced energy, in all forms, is needed to maintain our industrial productivity and high standard of living. Coal must provide a significant portion of our present and future energy requirements. 1976 production of mined bituminous and lignite coals was nearly 679 million tons. Energy planners believe this production level must be raised to 1.2 billion tons by 1985 to attain our national energy goals. This will require more numerous and more efficient coal mining, preparation, and transportation operations.

There are many difficult operations in coal mining; one of the most troublesome being the disposal of coal preparation wastes, in particular, the fines portion. Research by Dravo Lime Company has led to the application of an additive, Calcilox, that when added to waste solids, produces a stable material with the consistency of compacted soil. With these greatly improved characteristics, recognized disposal means can then be utilized for the fines.

Discussion

Generally, a coal preparation plant produces two types of refuse; a coarse fraction (plus 28 mesh), and a fine fraction (minus 28 mesh). These two wastes can be handled separately or mixed together based on the preparation plant circuitry and/or disposal criteria. Figure 1, Alternate Refuse Handling Modes, illustrates some typical disposal methods. Based on our experience, the coarse refuse, alone, does present serious disposal problems because of the size consist, low moisture, compactibility, and cohesive strength. These properties can be utilized in designing safe and environmentally acceptable landfill disposal sites.

However, the fine refuse is quite different and its disposal may not be straightforward. Typically, the fine refuse solids are in a slurry form ranging from 15% to 45% solids, by dry weight, or exist as a 55% to 75% thixotropic solids cake produced by a vacuum disc filter, solid bowl centrifuge, or a plate and frame filter press. In either a cake or slurry form, the solids are not readily dewatered further; will easily reslurry; and do not possess significant cohesive strength for permanent landfill disposal. The latest statistics indicate that the 1976 mined bituminous and lignite coal tonnage was 679 million tons with 269 million tons mechanically cleaned. It is estimated that the amount of refuse produced was 89 million tons consisting of 16 million tons as fines and 73 million tons as coarse refuse. An important underlying fact in dealing with the disposal of these quantities is that over 80% of the coal cleaning plants are located in the states of West Virginia, Kentucky,

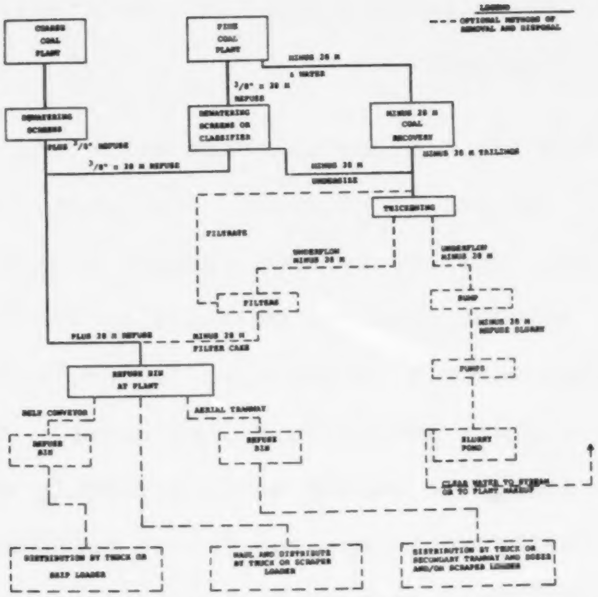

Figure - 1 ALTERNATE REFUSE HANDLING MODES

Pennsylvania, Virginia, Illinois and Ohio. In the coal producing regions of these states, the topography ranges from gently sloping to steeply mountainous; not conducive for landfill disposal of a fluid mass such as the fine coal refuse.

A common fines disposal method is to pump the thickener underflow to a lagoon and allow the solids to settle. When topography is favorable for the lagooning approach, several lagoons may be excavated to provide a long filling lifetime. After these ponds are full, they may be abandoned and new ones excavated. In the major Appalachian coal fields, topography usually does not favor extensive pond systems. Generally, a pond or two are excavated, filled, and the settled solids reexcavated and disposed of. The pond or ponds are then refilled, and the cycle repeated. The major problem with handling the settled fines is the fluidity of the material at normal settled solids concentration between 45% and 60% (Figure 2, Fluid Settled Solids). Due to the clayish nature of most fine refuse, the solids will easily reslurry even after the solids have been air dried.

As an alternate for ponds or impoundments, the thickener underflow may be mechanically dewatered to (1) close the plant water circuit, (2) save disposal space, and (3) attempt to improve the handling characteristics of the slurry. Assuming ideal success in all handling stages, the dewatered material

Figure - 2
FLUID SETTLED SOLIDS

could be mixed with the coarse refuse and compacted into a stable landfill. Unfortunately, this is a huge, seldom realized assumption. In actual practice, the cakes are extremely difficult to homogeneously mix into the coarse refuse. They remain in large, sticky masses which gum up conveyors, bins, and trucks. In summary, the dewatered fines, whether intact or partially mixed with the coarse material, present a troublesome handling and disposal task.

We believe that the disposal of these fine refuse solids can be dramatically improved. One viable solution is the addition of a chemical, Calcilox additive, to the refuse slurry or dewatered cake. Calcilox additive (Figure 3) is a dry, free-flowing light grey powder of inorganic origin and it is chemically activated with water. Calcilox additive is mixed into the refuse on a weight percentage of the dry refuse solids. The net result of this addition will be the development of definitive engineering properties in the refuse; such as compressive strength, cohesion, shear resistance, and reduced water permeability.

The most recent technical study(1) has just been completed for the Pittsburgh Branch of the Department of Energy

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(1) Management of Coal Preparation Fine Wastes Without Disposal Ponds, D. C. Hoffman, R. W. Briggs, S. R. Michalski, Dravo Lime Company, June 15, 1978, Contract No. J0177050, Department of Energy, Branch of Procurement, Washington, D.C.

Figure - 3 CALCILOX, A DRY FREE FLOWING POWDER (formerly the United States Bureau of Mines) investigating the general effects of chemical stabilization on fine coal refuse. Fine refuse samples were collected from various preparation plants representative of "typical" operations in the Eastern bituminous coal fields. One of the prime objectives of study was to investigate the untreated, as-received properties of these fine solids. Table I, Untreated Fine Coal Refuse, tabulates the important physical properties of permeability and direct shear results for the samples tested as a settled slurry and as a filter cake. In reviewing the data, it must be pointed out that the solids content of the slurries and cakes is quite high due to the laboratory conditions. Field investigations indicate that settled solids usually run between 45% and 60% solids while mechanically dewatered cakes may range from 55% to 75% solids. The major points illustrated here are the overall lack of any cohesive strength (less than 1 psi) and low permeabilities (10^{-6}) on both the settled solids and filter cakes. These two factors contribute quite heavily to the fluidity of large masses of fine coal refuse.

The chemical additives tested in this study were hydrated lime, Portland Type 1 cement, and Calcilox additive. Lime and Portland cement have been known to impart some stabilizing effects to fine refuse but no quantitative results have been reported. Secondly, all three additives are commercially

TABLE I

UNTREATED FINE COAL REFUSE

Sample No.	Permeability				Direct Shear										Consolidation
	Settled Slurry		Filter Cake		Settled Slurry					Filter Cake					
	cm/sec.	Solids[1] (%)	cm/sec.	Solids (%)	Consolidated Density (Lb/Ft^3)	Degree of Saturation (%)	ø[2]	Cohesion (psi)	Solids (%)	Consolidated Density (Lb/Ft^3)	Degree of Saturation (%)	ø[2]	Cohesion (psi)	Solids (%)	Compression Index (C_c)
1104	6.0×10^{-6}	71.7	5.1×10^{-7}	76.8	69.6	84.7	10°	0.018	73.7	74.8	90.7	22°	0.200	75.4	0.19
1105	1.0×10^{-5}	73.1	4.1×10^{-6}	77.0	66.4	76.7	51°	0.218	78.4	50.6	60.2	36°	0.309	71.7	0.12
1106	7.4×10^{-6}	76.0	4.8×10^{-6}	79.6	71.1	98.9	53°	0.173	80.5	56.1	51.3	30°	0.182	80.2	0.09
1107	2.6×10^{-6}	79.6	1.3×10^{-6}	82.5	75.8	78.0	34°	0.036	80.3	79.2	72.2	38°	0.791	83.3	0.11
1110	4.4×10^{-6}	65.4	1.6×10^{-6}	73.0	58.1	94.2	20°	0.073	69.5	62.1	98.7	29°	0.045	71.8	0.15
1111	4.1×10^{-6}	67.3	1.4×10^{-6}	75.9	65.2	97.8	37°	0.045	72.6	69.9	88.9	42°	0.245	77.8	0.17
1112	1.9×10^{-5}	71.2	6.2×10^{-6}	82.0	62.1	98.4	22°	0.327	79.7	68.6	100.0	28°	0.255	84.6	0.15
1113	4.2×10^{-6}	64.9	2.0×10^{-7}	74.5	62.1	100.0	11°	0.100	68.7	62.1	100.0	14°	0.218	70.8	0.19
1114	5.5×10^{-6}	65.0	8.1×10^{-7}	74.0	68.2	100.0	8°	0.055	72.6	68.0	89.5	21°	0.082	72.8	0.18

[1] Solids = % Dry Wgt.

[2] Angle of Internal Friction

[3] Settled Slurry

available and are competitively priced. Based on Dravo's experience, the most economic use of chemical stabilization techniques occurs with additive dosages ranging from 5% to 15%, on a dry solid basis, high solids cakes to thickener underflows, respectively. With this in mind, stabilization tests were conducted covering the range of typical thickener underflows (25% to 35% solids) and high solids filter cakes (70% to 82% solids).

The procedure used to evaluate the effectiveness of each additive was the development of unconfined compressive strength after 40 days of curing. Table II, 40-day Unconfined Compression Strength, lists the results obtained for ambient temperature stabilization. Using the criterion of highest possible strength, this figure illustrates that Calcilox additive is the best for treating thickener underflows in the 25% to 35% solids range. In seven out of the nine filter cake samples, Calcilox is also superior to Portland cement and in all cases, vastly superior to lime additions. In actual applications, the dosage level and strength desired will vary and is dependent on each specific disposal mode and can be verified by laboratory testing.

Recommended Stabilization Methods

Thus far, we have attempted to define fine coal refuse disposal and to present the latest laboratory results. The

TABLE II
40-DAY UNCONFINED COMPRESSION STRENGTH
(PSI)

Treatment		Sample Number								
		1104	1105	1106	1107	1110	1111	1112	1113	1114
Additive	Mixed Solids %	72°(1)	72°	72°	72°	72°	72°	72°	72°	72°
Untreated	25	*(2)	*	*	*	*	*	*	*	*
	35	*	*	*	*	*	*	*	*	*
	FC(3)	*	6.6	*	*	*	*	5.1	*	*
5% Portland Type I	35	*	*	*	*	*	*	*	*	*
	FC	95.9	85.0	73.9	123.2	18.7	67.6	50.5	60.4	67.1
5% Lime	35	*	*	*	*	*	*	*	*	*
	FC	37.2	23.1	20.0	23.2	7.6	*	8.5	9.6	15.6
5% Calcilox A	35	*	8.8	8.5	10.0	0.8	1.6	4.8	1.4	2.0
	FC	78.6	124.9	80.3	218.2	81.3	50.7	98.5	106.9	89.1
5% Calcilox B	35	*	7.2	4.9	7.5	1.4	2.6	10.2	1.5	2.0
10% Portland Type I	25	*	*	*	*	*	*	*	*	*
	35	1.6	0.8	2.8	*	*	*	*	0.9	*
	FC	141.3	165.3	141.0	76.1	115.5	141.5	159.4	160.9	145.4
10% Lime	25	*	*	*	*	*	*	*	*	*
	35	*	*	*	*	*	*	*	*	*
	FC	39.8	12.6	22.2	15.2	16.4	13.6	13.3	14.6	16.1
10% Calcilox A	25	6.1	39.4	19.7	20.6	5.4	9.0	7.7	3.7	4.7
	35	15.1	27.0	33.9	38.9	10.8	14.1	4.5	8.4	4.4
	FC	368.6	188.5	494.4	233.7	120.0	116.6	69.9	231.2	224.5
10% Calcilox B	35	10.3	37.5	36.1	32.8	19.5	12.2	33.7	16.4	6.8
15% Portland Type I	25	*	*	1.9	*	*	*	*	*	*
	35	4.5	2.2	3.6	*	1.9	*	*	1.9	*
15% Lime	25	*	*	*	*	*	*	*	*	*
	35	*	*	*	*	*	*	*	*	*
15% Calcilox A	25	15.4	31.0	80.6	47.7	12.1	15.5	6.6	10.3	11.6
	35	24.4	30.2	59.4	35.7	17.1	21.0	13.3	24.2	15.0
15% Calcilox B	35	35.9	86.1	80.3	87.9	34.4	26.4	39.3	39.5	24.0

(1) Curing temperature measured in degrees Fahrenheit.

(2) * Indicates specimen did not have a measurable strength at 40 days.

(3) FC - Filter cake solids level - 70%-82% Solids

following represents disposal modes that can be utilized for full-scale operations.

1. Interim Stabilization (Figure 4)

Fine refuse thickener underflow is treated with Calcilox additive and deposited into temporary curing ponds. The duration of the curing period will vary from days to several weeks depending upon the nature of the refuse, the Calcilox additive dosage, the slurry solids etc. When the handling characteristics of the slurry are sufficiently improved, it is excavated by dragline or other methods and is transported to a permanent landfill disposal site. By using the correct amount of Calcilox additive and excavating the material before the reaction has produced a very rigid mass, it is possible to continue the hardening after the material is placed in its final disposal location. This alternate requires some space and due to multiple handling, does represent a relatively higher operating cost than the following methods 2, 3, or 4. Operating costs are compensated for by increased operational flexibility and control. In addition, supernatant can be easily reclaimed for reuse in the preparation plant.

2. High Solids Cake - Separate Disposal (Figure 5)

For those companies which already own mechanical dewatering equipment, it is possible to treat the resulting

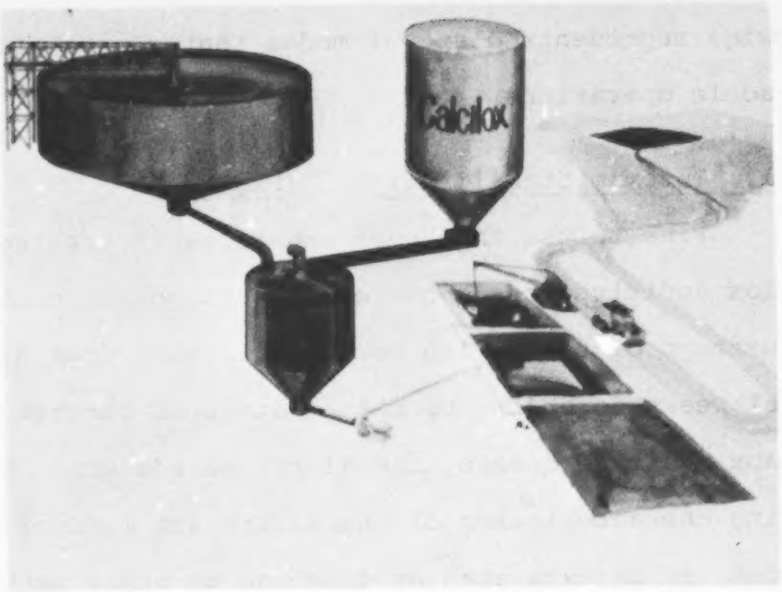

Figure - 4
INTERIM STABILIZATION

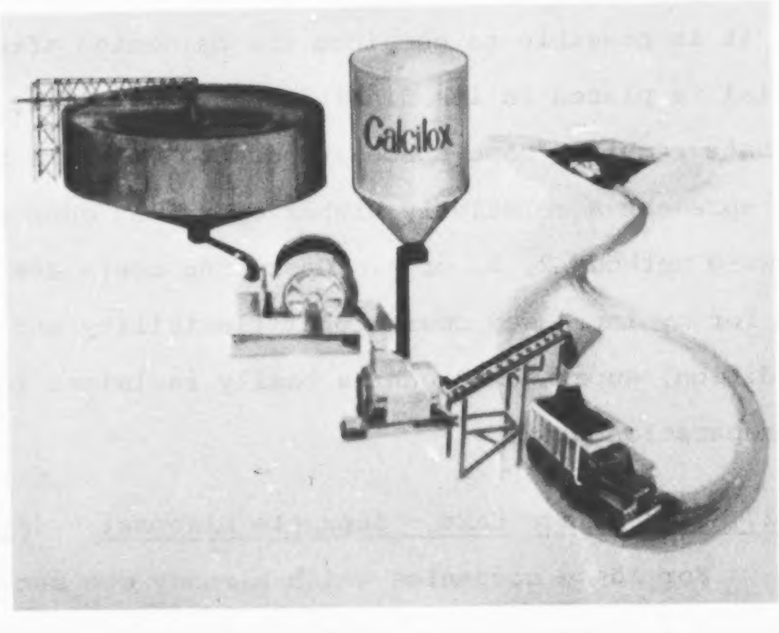

Figure - 5
HIGH SOLIDS CAKE - SEPARATE DISPOSAL

cakes at a somewhat lower additive cost than would be the cost for stabilizing thickener underflow. It is possible to excavate small pockets or lagoons within the coarse refuse deposit. Treated cake is retained in these pockets until the Calcilox additive has hardened the material sufficiently to support earthmoving equipment. The pocket can then be graded, compacted, and covered with coarse refuse. Stabilization rates for cakes are rapid so that these pockets can be covered quickly if required for the management of the landfill. Again, this method offers some flexibility, and lower operating costs when compared to interim ponding. This "pocket" method does not appear to be suitable for thickener underflows unless the coal company can construct large enough pockets to meet the longer stabilization periods. In addition, the costs of a mobile and flexible piping system may be prohibitive.

3. High Solids Cake-Coarse and Fine Refuse Disposal (Figure 6)

The third disposal mode, mixing coarse and Calcilox additive treated fines, may be the most easily adapted to an existing plant that currently combines a dewatered fine refuse with the coarse reject. In most plants the amount of coarse refuse (by weight and volume) is several times the amount of fine refuse. However, the combination of the two generally creates a nearly unmanageable situation in terms of immediate handling and long-term stability. After laboratory testing of the fine refuse cake with Calcilox additive, an optimum

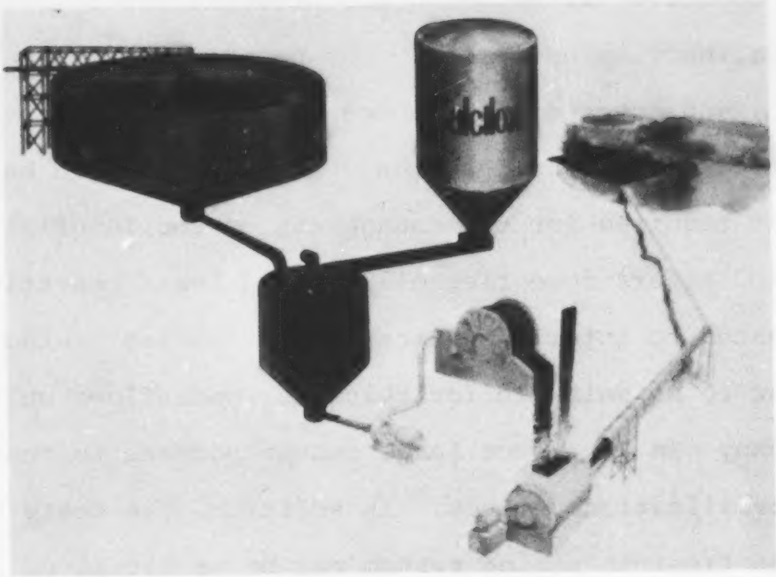

Figure - 6
HIGH SOLIDS CAKE - COARSE AND FINE REFUSE DISPOSAL

dosage is determined. Subsequent laboratory testing of mixtures of coarse refuse and treated fine refuse cake can determine the proper ratio of coarse to fine refuse for immediate handling properties. The addition of Calcilox additive to the fine refuse cake and mixing with the selected coarse fraction will give satisfactory, immediate handling characteristics plus long-term stability. The primary disadvantage of this approach is the extra cost of sizing and blending equipment to handle the whole plant reject while only the fines are the problem.

4. Permanent Impoundment Stabilization (Figure 7)

Fine refuse slurry is treated with Calcilox additive and pumped behind an impoundment where it settles and hardens. For those companies that already own, or are convinced that they should construct, lagoons or impoundments for thickener underflows, we believe that the superior properties of Calcilox additive stabilized slurries might afford savings in impoundment construction, and could greatly reduce abandonment procedures. Several advantages, tangible and intangible, for this type of operation could be:

A. Reduced initial capital outlay for dam construction.

B. Construction costs of the dam might be lower if retaining wall structural considerations are used.

C. Impoundment would not be holding a fluid, but a rigid mass.

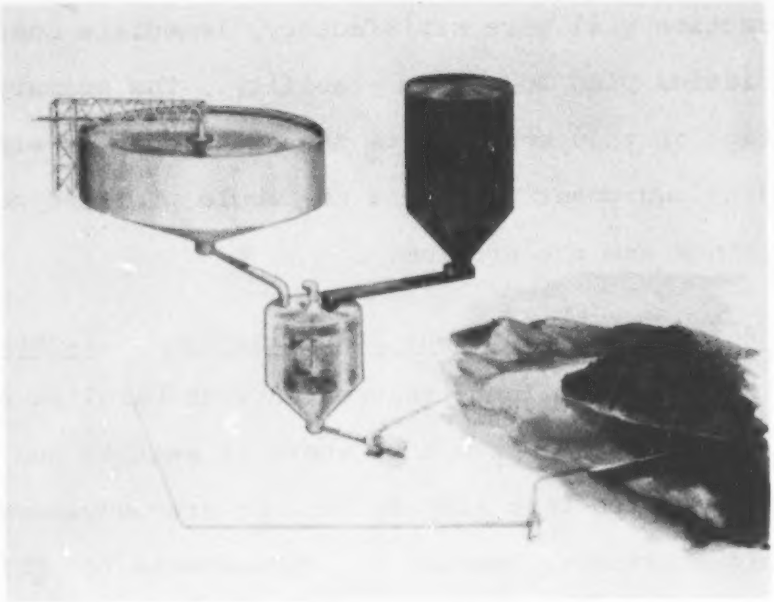

Figure - 7
PERMANENT IMPOUNDMENT STABILIZATION

D. No devastating fluid mass movements could occur.

E. The impoundment offers an emergency reservoir to which wastes can be dumped conveniently in the event of an operating emergency in the preparation plant.

Full-Scale Systems

In employing Calcilox stabilization of fine coal refuse, the overall justification finally becomes one of economics. It is very important to emphasize that many costs associated with current disposal practices are obscure, since they are included in other mine operations. Secondly, some factors that readily affect a disposal operation are very intangible and hard to equate to dollars and cents. Important considerations are (1) the cost of maintaining private and public roads due to slopping of fine refuse; (2) the time involved in pulling equipment out of the muck; (3) low morale due to bad working conditions - long hours in a messy environment and (4) the constant threat of complete facility shutdown due to regulatory spot checks. In a complete economic evaluation of disposal costs, the above items plus others must be considered whether Calcilox is being evaluated or not.

Currently, Calcilox additive stabilization techniques are in various stages of investigation by numerous companies representing nearly 60,000 tons per day of cleaning capacity. Refuse disposal modes under investigation will utilize vacuum disc filter cakes, solid bowl centrifuge cakes, and thickener underflows to meet the specific objectives of the client companies. At this time, three Calcilox additive stabilization systems are in various stages of final construction, start-up, and/or operation. All three are treating slurries ranging from 15% to 45% solids and are employing the interim pond stabilization method with subsequent dry landfill disposal with the remaining plant refuse. The following is an example of one of these systems now in operation (the dollars shown are 1977 dollars).

Example 1: Disposal Mode - Interim pond disposal with subsequent excavation and combination with remaining plant refuse.

Coal Use - Steam

Cleaning Capacity - 1300 TPH

Clean Coal - 1000 TPH

Fines Disposal Mode - 40 TPH (400 gpm @ 30% solids) as thickener underflow and 40 TPH as filter cake combined with coarse.

Current Overall Fines Disposal Costs per Ton Clean Coal. . $1.52

Approximate Calcilox System Capital Installed Cost . . . $80,000

Approximate Calcilox Additive Dosage - 10%

Estimated Overall Fines Disposal Costs with Calcilox Stabilization per ton Clean Coal $1.13

Estimated Net Disposal Savings with Calcilox Stabilization per ton Clean Coal $0.39 (25%)

Estimated Calcilox Additive Cost per ton Clean Coal. . . . $0.32 thickener underflow only
$0.46 for all fines

Figure 8, Calcilox Additive System, depicts the actual installed treatment system. Briefly, the thickener underflow enters the mix tank installed below a 100 ton Calcilox storage silo. The Calcilox is metered into a waste slurry slipstream via a prewetting cone with a variable speed rotary valve. The mix tank is equipped with a twin-blade turbine agitator to quickly disperse the Calcilox throughout the mix tank and to maintain a uniform solids suspension. The mix tank is sized to allow for a 10 to 20 minute retention time for all the anticipated thickener underflow rates. The treated slurry is then pumped to the interim settling ponds for 30 days curing before excavation and dry landfill disposal with the remaining plant refuse. The system is also equipped with various ancillary devices to maintain uniform tank levels, bulk Calcilox feed densities, and to assure safe and environmentally acceptable operation of the system.

In this brief discussion, Calcilox additive stabilization technology has been reviewed, stabilization methods presented, and an actual Calcilox treatment system shown with its associated costs. In stating these particular costs and for estimating others, it should be reemphasized that the justification for a Calcilox system involves costs that are tangible and, to a great extent, intangible. A valid economic justification for Calcilox stabilization should start with a thorough investigation of your current fine coal refuse disposal costs.

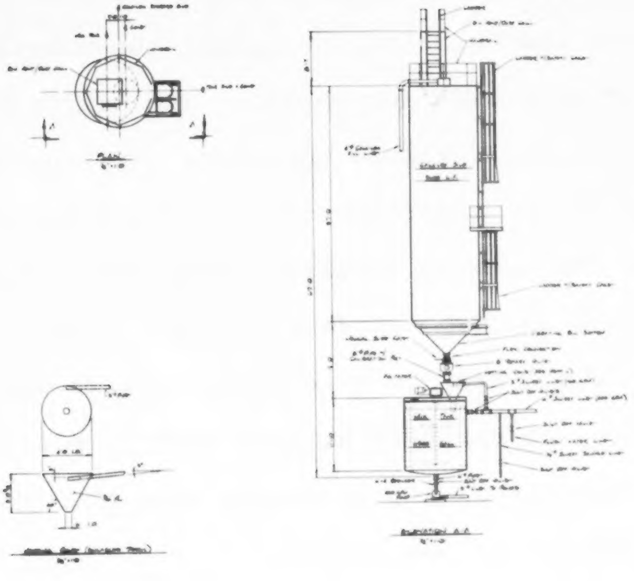

Figure - 8
CALCILOX ADDITIVE SYSTEM

Important items that should not be overlooked in evaluating these disposal costs are: (1) lost or reduced production due to disposal problems; (2) possible reduction of flocculents used for additional dewatering in settling ponds, filters, or centrifuges; (3) elimination of additional and/or special equipment needed to maintain the disposal operation; and (4) possible resale or reclamation of the Calcilox additive stabilized fine coal refuse. This last point may be quite applicable to refuses that possess a net BTU content in excess of 5000 BTU/lb. Thus, with all these cost factors evaluated, a sound economic decision can be made on the application of Calcilox additive stabilization techniques for fine coal refuse disposal.

CHEMICAL AND BIOLOGICAL CHARACTERIZATION OF LEACHATE FROM COAL CLEANING WASTES

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ABSTRACT

Two coal-cleaning solid wastes--a low sulfur residue (LSR) and a high sulfur residue (HSR)--from the Illinois Herrin (No. 6) coal member were characterized mineralogically and chemically. The chemical solubility, attenuation by soil, and toxicity of soluble constituents in a series of aqueous leachate solutions at several pHs were determined.

The major chemical constituents of the solid residues were Al, Ca, Fe, K, S, and Si (>1%). Ba, Cl, F, Mg, Mn, Na, Sr, Ti, and Zn were present at concentrations between 100 and 10,000 ppm. Trace metals present in the residues at concentrations between 10 and 100 ppm included As, Co, Cr, Cu, Pb, and Ni; 20 additional elements were found at concentrations less than 10 ppm. Mineralogically the coal-cleaning wastes were similar; both included illite, kaolinite, quartz, calcite, and Na-Ca feldspars. The notable exception was the large pyrite concentration in the HSR.

Of the 60 chemical constituents determined in the solid wastes, 17 from HSR and 20 from LSR were found to be soluble enough to exceed recommended water quality levels within the pH range studied (2.5 - 9.2) and under these laboratory test conditions. Most of these were soluble only when the pH was quite acid. Three constituents in the HSR leachates (K, NH_4, and SO_4) exceeded recommended water quality levels in leachates of all pHs, while no constituents in the LSR exceeded recommended levels at all pH values.

The attenuation study employed the dispersed soil methodology using three widespread Illinois soils of varying character. Results showed a high degree of attenuation of the major constituents; however, elution of Mg from the soils themselves could possibly present the greatest potential for pollution from land disposal.

Ninety-six-hour static bioassays were conducted with young fathead minnows (Pimephales promelas) to determine the toxicity of these wastes leachate solutions. Full-strength acidic leachates were acutely toxic and neutral leachates were relatively nontoxic. However, acidic solutions of HSR that were neutralized by dilution were still found to cause mortality. This suggests a source of toxicity other than acidity.

INTRODUCTION

In the United States almost 3 billion tons of carbonaceous mineral wastes have accumulated as a result of coal mining (National Academy of Sciences, 1975). With the projected increase in coal as an energy source, the wastes are also projected to increase. Of primary concern is the pollution potential of these accumulations of coal waste. Regardless of how these wastes are disposed of, they will eventually be exposed to leaching processes that may make the soluble constituents available to the environment. In the case of pyritic wastes, the pollution potential increases due to the production of sulfuric acid and its subsequent solubilization of metals. This increased acidity may affect both the productivity of streams and lakes (Kemmel and Sharpe, 1976) and the fertility of the land around waste disposal sites (National Academy of Sciences, 1975).

In order to ascertain the pollution potential of coal refuse, it is desirable to determine: (1) the chemical and mineralogical character of the solid waste, (2) the soluble phase of the solid waste, (3) the attenuation characteristics in the environment of the soluble constituents, and (4) the toxicity to biota of these soluble constituents.

Characterization of the Coal Cleaning Wastes

Current Studies

This project is part of ongoing research by the Illinois State Geological Survey to characterize coal and coal residues (Ruch, Gluskoter, and Kennedy, 1971; Ruch, Gluskoter, and Shimp, 1973; Ruch, Gluskoter, and Shimp, 1974; Gluskoter, 1975; and

Gluskoter et al., 1977). Included in this work is an analysis of the pollution potential of coal solid wastes (Griffin et al., 1977). The wastes being studied include liquefaction residues (SRC and H-coal), Lurgi gasification ashes, fly ash, water quenched slag, high and low temperature chars, and high and low sulfur cleaning wastes (gobs). This report deals with the results from the coal cleaning wastes and represents a small portion of the overall project. The authors reserve the right to revise interpretation of data upon completion of the project.

Chemical and Mineralogical Characterization

Two coal cleaning solid wastes—a low sulfur (LSR) and a high sulfur residue (HSR)—from the Illinois Herrin (No. 6) coal member were characterized chemically and mineralogically. The chemical composition of the two wastes has been determined for approximately 60 constituents (Table 1). The major chemical constituents of the solid residues were Al, Ca, Fe, K, S, and Si (>1%). Barium, Cl, F, Mg, Mn, Na, Sr, Ti, and Zn were present in the residues at concentrations between 100 and 1000 ppm. Trace metals present in the residues at concentrations between 10 and 100 ppm include As, Co, Cr, Cu, Pb, and Ni.

Mineralogically the coal cleaning wastes are similar; both included illite, kaolinite, quartz, calcite, and Na-Ca feldspars. The notable exception was the large pyrite concentration in the HSR. The mineralogy was determined by X-ray diffraction, scanning electron microscope, optical techniques, and chemical methods.

Aqueous Solubility

The solubility of constituents in the residues was determined

Table 1: Chemical Characterization of the Coal Cleaning Waste

Constituent	Solid ash content (mg/kg) LSR	HSR
Ag	0.03	0.20
Al	97,008	56,572
As	68	13
B	200	9.3
Ba	400	300
Be	3	2
Br	3.2	1.2
Ca	21,227	28,159
Cd	<1.8	<1.4
Ce	100	92
Cl	700	300
Cr	78	45.3
Co	13	10.3
Cu	36	29
Cs	15.2	9.6
Eu	1.5	1.2
F^-	900	1,105
Fe_{total}	24,813	86,157
Ga	19	11
Ge	4.1	1.2
Hf	7.9	3.2
K	17,102	9,962
La	50	43
Lu	0.43	0.42
Mg	3,859	1,869
Mn	310	310
Mo	<1	3.2
Na	3,635	2,419
Ni	55	48
Pb	55	55

Table 1: (cont'd)

	Solid ash content (mg/kg)	
Constituent	LSR	HSR
P	1,397	829
Rb	200	100
S_{total}	5,100	108,800
$S_{pyritic}$	4,600	76,100
Sulfate	400	13,500
Sb	2.7	0.2
Sc	15.2	9.1
Si	261,380	145,490
Sm	8	6.9
Sn	7.2	3.3
Sr	79	100
Ta	1.2	0.8
Te	2.2	0.6
Th	20	13
Ti	8,298	4,668
Tl	8.0	8.2
U	3.1	2.9
V	39.3	35.3
W	2.9	2.5
Yb	4.3	2.1
Zn	500	300
Zr	200	100

by making 10% aqueous slurries. Duplicate sets of four slurries each were adjusted to four individual pH values over the range of 2.5 to 9.2. Glass carboys (2.5 gal) were employed as reaction vessels. One of the duplicate sets was equilibrated under an argon (oxygen- and CO_2-free) atmosphere and the other set was equilibrated under an air (oxidizing) atmosphere. The pH values were monitored and readjusted to the specified values when necessary. The slurries were monitored for 3 to 6 months or until the solution pH remained constant, at which time chemical equilibrium was assumed.

Tables 2 and 3 list the elements from the solid residues that were soluble enough to exceed recommended water quality levels under the laboratory test conditions. The analyses were performed by atomic absorption and colorimetric techniques (EPA Methods, 1974). Table 2 compares the waste leachates at their natural pHs and under both types of atmospheres. Table 3 compares the leachates at their adjusted acidic pHs. Only K, NH_4, and SO_4 exceed the recommended levels in the HSR leachates at all pHs, while no constituents of the LSR leachates exceeded recommended levels at all pH values. The values listed in Table 3 represent what might be expected under acid mine drainage (AMD) conditions. It is unlikely that AMD would develop for the LSR waste due to its relatively low sulfur content (0.5%) compared to the HSR waste (10.8%). However, AMD did not develop for the HSR waste under the experimental conditions described above, and Table 3 represents only the result of adjusting the leachate pH with nitric acid. The concentrations in solution obtained by this adjustment fall well within the range of values others have reported for typical AMD affected streams

Table 2: Constituents Exceeding Recommended Water Quality Levels in the Natural pH Supernatents under the Laboratory Test Conditions (concentration in mg/l)

	Low Sulfur Residue		High Sulfur Residue		
Constituent	Air pH 8.6	Argon 8.5	Air 7.5	Argon 7.4	Recommended Water Quality Levels
Al	4.4	0.62	--	--	0.1
B	1.0	1.0	--	--	0.75
Ca	--	--	480	590	50
F	1.7	1.7	1.4	1.4	1.0
K	--	--	11.9	15.5	5.0
Mn	--	0.07	--	--	0.05
NH_4	--	--	0.3	1.5	0.02
Pb	0.15	--	0.2	0.15	0.03
PO_4	0.08	0.06	--	--	0.05
SO_4	--	--	1600	1500	250

Table 3: Constituents Exceeding Recommended Water Quality Levels in the Most Acid pH Supernatents under the Laboratory Test Conditions (concentration in mg/l)

Constituent	Low Sulfur Residue Air pH 2.5	Low Sulfur Residue Argon pH 2.4	High Sulfur Residue Air pH 2.6	High Sulfur Residue Argon pH 2.5	Recommended Water Quality Levels
Al	29.0	57.0	27.6	35.3	0.1
Ba	1.9	2.5	--	--	1.0
Ca	2595	2784	2310	2305	50
Cd	0.09	0.09	--	--	0.01
Cr	0.06	0.13	0.09	0.07	0.05
Co	0.64	0.48	0.90	0.82	0.05
Cu	1.68	1.34	--	--	0.2
Fe_{total}	130	360	205	275	0.3
K	38	40	19	20	5
Mg	119.7	138.9	68.7	70.4	50
Mn	24.4	30.7	17.4	18.0	.05
NH_4	4.5	4.9	3.8	4.2	.02
Ni	1.06	--	1.45	1.57	1.0
Pb	0.50	0.70	0.40	0.50	0.03
PO_4	3.0	44.0	2.0	13.5	0.05
SO_4	--	--	1300	1400	250
Zn	1.55	1.40	3.7	3.1	0.2

(Wilmoth, 1972; Hanson, 1972; and Gang and Langmuir, 1974). The most probable explanation is inadequate oxidation due to the slow diffusion rate of air through water in the 2½ gallon carboys employed. Other possible explanations are the lack of ferric iron in solution as a pyrite oxidizer and insufficient development of bacterial activity.

It is difficult to explain the aqueous chemistry of a complex system such as the coal refuse leachates. Possible complexation, ion pair formation, and the effects of organic components on the formation of organometallic complexes hinders the description of these systems. However, it is still of interest to examine them in an effort to account for their soluble components, and of most interest is the iron and sulfate chemistry.

Figure 1 is a plot of the Ca^{2+} and $SO_4^{=}$ ion activities for the two aerated leachate systems. The plot indicates that, while the LSR leachates are undersaturated with respect to gypsum/annhydrite, the HSR leachates are slightly supersaturated in all but the most alkaline case. However, because of the range of error in sulfate analyses and the use of solubility products calculated for pure $CaSO_4$ systems, it is quite possible that the HSR leachates are within the range of saturation and are indeed in chemical equilibrium with annhydrite. Further calculations show that Ba and Sr in the LSR leachates are undersaturated with respect to their sulfate compounds with approximately 100% of the Ba and Sr in the solid waste being in solution. The HSR solutions are also undersaturated with respect to $SrSO_4$, where approximately 50% of the available Sr in the refuse is in solution.

Figure 2 is an Eh vs. pH diagram displaying the stability relations of iron oxides and sulfides in water (Garrels and Christ,

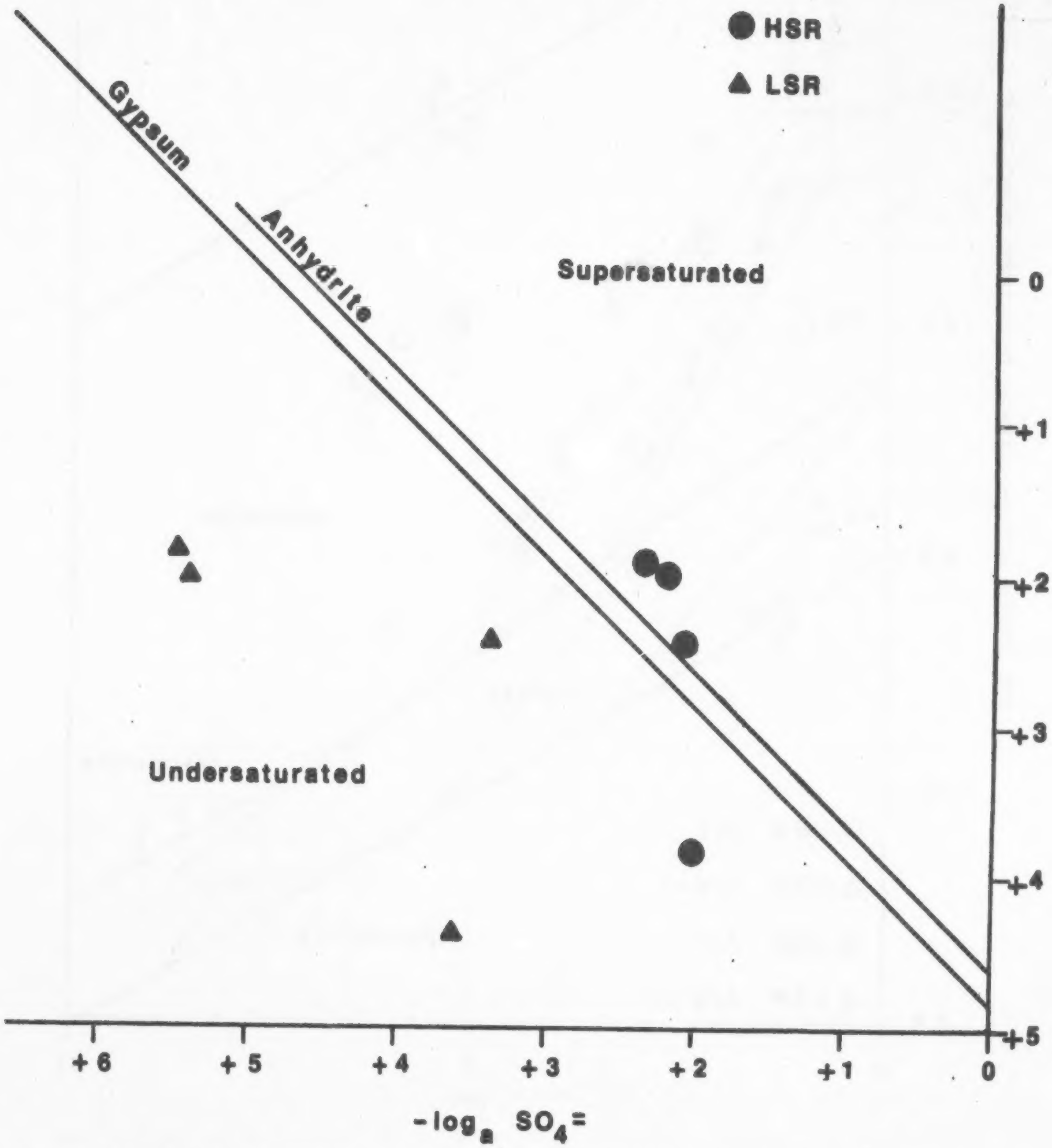


Figure 1: Plot of calcium sulfate solubilities for aerated HSR and LSR.

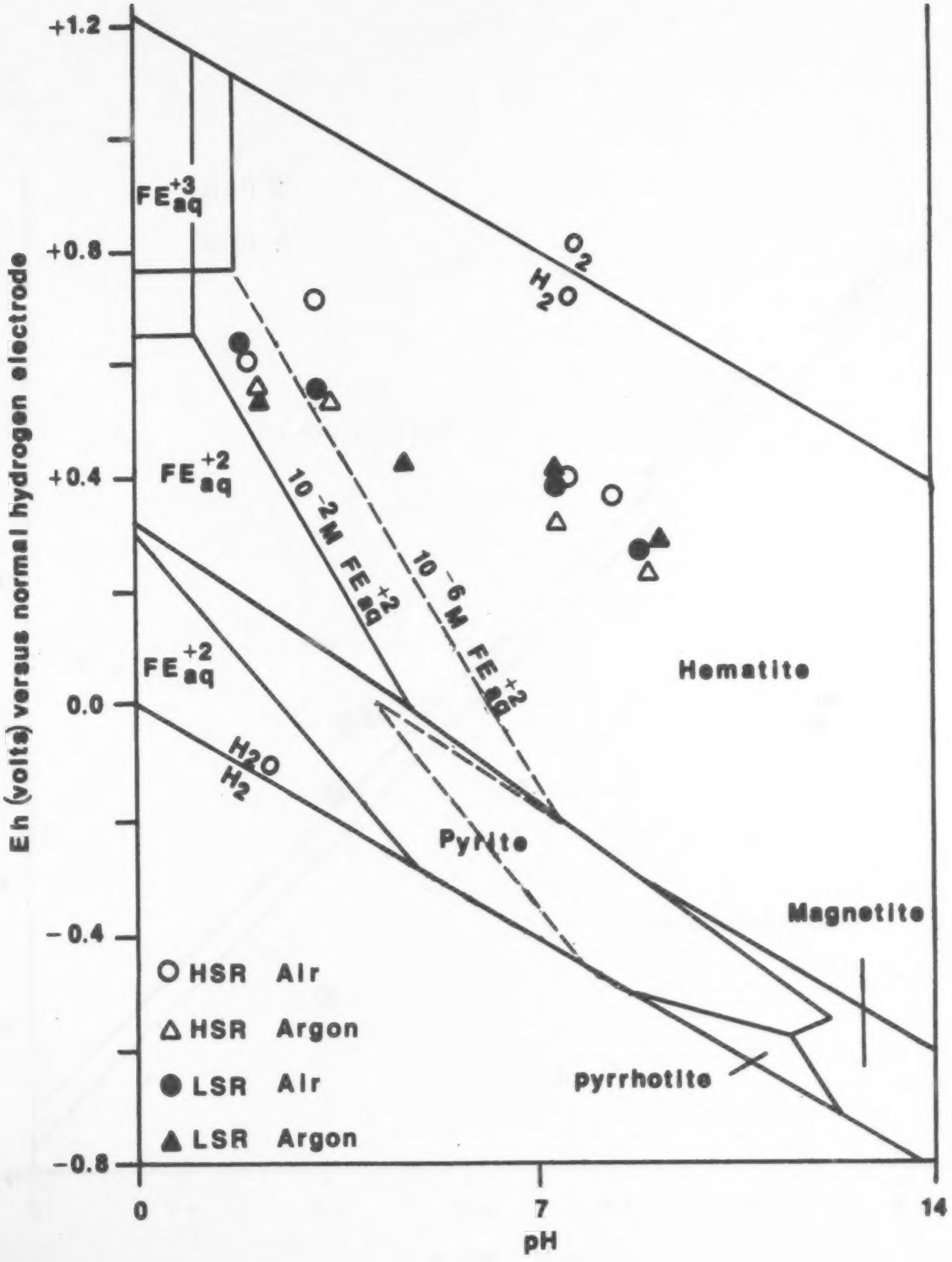


Figure 2: Stability relations of iron oxides and sulfides in water at 25°C when $\Sigma S=10^{-3}$ molar (native sulfur field excluded).

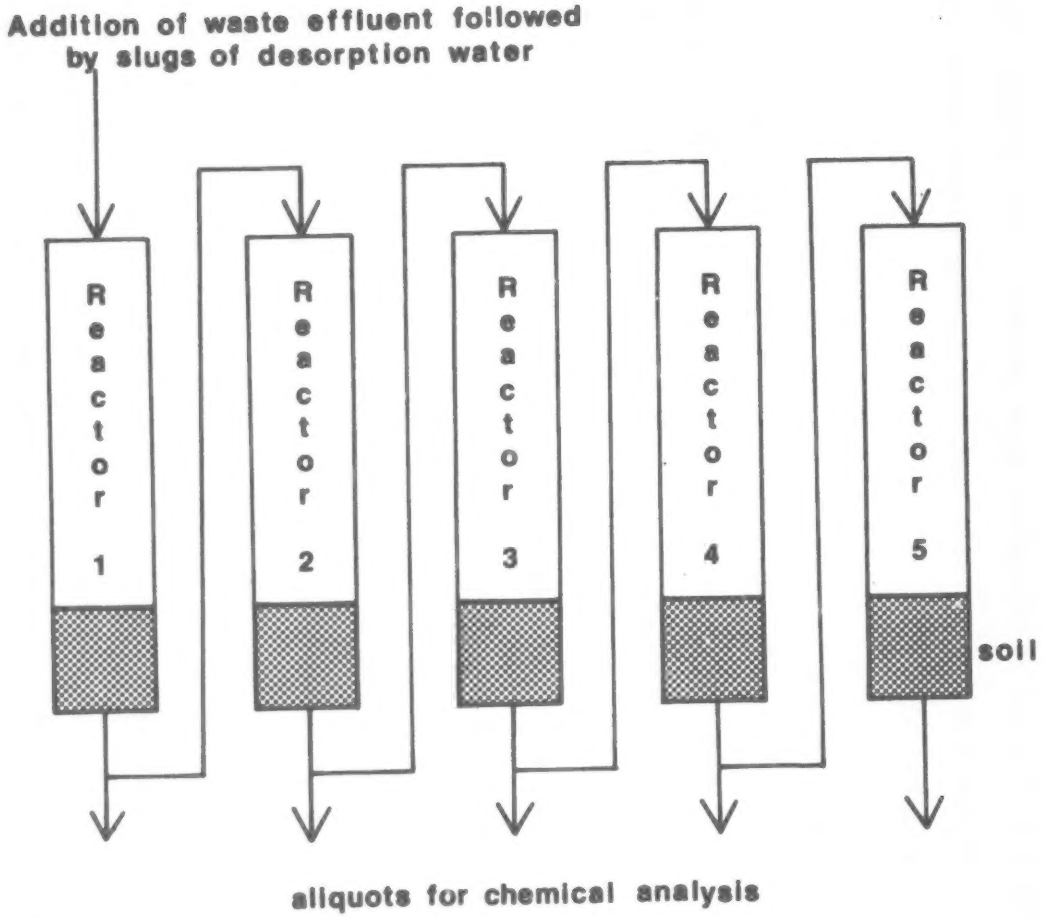
1965). There is a strong agreement between the Eh-pH values plotted for the leachates and the Fe^{2+} concentrations that were measured experimentally. However, it is of interest to note that the leachate systems (under both air and argon) are in the Fe^{2+}-hematite stability range. This indicates that the leachate systems are not in equilibrium with pyrite. The reason for the lack of equilibrium is the slow rate of pyrite dissolution (oxidation) as discussed above.

Attenuation Study

The traditional approach to studying earth material attenuation of leachates or waste effluents has been experimentation using soil column leaching. Rovers, Mooij, and Farquhar (1976) have shown that a dispersed soil methodology or batch reactor technique was suitable to approximate the behavior of contaminants of liquid industrial wastes in soils at a considerable savings in time and expense over soil column leaching studies.

The dispersed soil method has been shown to produce similar results to both remoulded and undisturbed column leaching studies (Rovers, Mooij, and Farquhar, 1976). The technique involves mixing a known volume of leachate with a known weight of soil brought to field moisture capacity. This is repeated five times in series with portions of leachate being drawn off and filtered for analysis. Figure 3 is a schematic diagram of the methodology.

Three Illinois soils, Ava sicl., Catlin sil., and Bloomfield ls., having a range of physical and chemical characteristics were collected and characterized for use in this study. Table 4 gives some of the pertinent characteristics of these soils.



Addition of waste effluent followed by slugs of desorption water
Reactor 1
Reactor 2
Reactor 3
Reactor 4
Reactor 5
soil
aliquots for chemical analysis

Figure 3: Schematic diagram of dispersed soil methodology.

Table 4: Soil Characteristics

Soil	pH	CEC (meq/100g)	Surface Area, N_2 $(m^2/g)^2$	Organic Carbon (%)	Sand (%)	Silt (%)	Clay (%)
Catlin silt loam	7.1	18.1	10.1	4.73	11.6	60.9	27.2
Ava silty clay loam	4.5	13.1	28.3	1.18	2	69.6	28.4
Bloomfield loamy sand	5.7	0.8	1.7	0.21	82	10	8

Only the natural pH supernatents are reported (LSR, pH 8.64 and HSR, pH 7.46). The filtrates from the attenuation study were analyzed for Al, B, Ca, Fe, K, Mg, Mn, Na, SO_4, and Zn. These ten constituents were determined because they were present in the leachates in sufficient concentration to present a potential pollution hazard due to leaching through soil.

Mechanisms of attenuation for the leachate constituents include adsorption, ion exhcange, complexation, precipitation, oxidation-reduction and many physical and biological mechanisms such as filtering and degradation. Usually attenuation in a complex system is a result of not just one but several of these possible mechanisms (Phillips and Nathwani, 1976). In general adsorption and precipitation are the principal mechanisms for removal of organic constituents. Also, the higher the clay and/or organic content of a soil the more effective the material is as an attenuating medium.

Tables 5 and 6 list the results of the attenuation analyses. The LSR leachate-soil mistures resulted in elution of Ca, K, and Mg from the three soils and Mn from the Ava soil. Only Na was consistently removed from solution. The HSR leachate-soil mixtures (Table 6) also resulted in elution of Mg but to a lesser extent and again elution of Mn from the Ava soil. All other constituents were attenuated.

The overall attenuation and elution of potential contaminants for the mixtures follows the same trend as the cation exchange capacity of the soils: Catlin $\geq$ Ava > Bloomfield. However, it is doubtful that exchange is the only mechanism responsible for removal. In the HSR leachate-soil mixtures, Ca^{2+} and $SO^{4=}$ are in

Table 5: Results of Attenuation Analysis for LSR Including Original Leachate Concentrations[a]

Constituent	Waste leachate	Ava	Bloomfield	Catlin
pH	8.6	4.2	6.7	6.9
EC[b]	0.74	0.36	0.62	0.73
Ca	1.8	5.5	20.7	47.5
K	3.8	5.6	9.9	6.6
Mg	4.6	113.0	70.4	231.0
Mn	<.03	0.33	<.03	<.03
Na	200	36	104	17
SO_4	112	44	102	139

[a] Concentrations in mg/l

[b] millimhos/cm

Table 6: Results of Attenuation Analysis for HSR Including Original Leachate Concentrations[+a]

Constituent	Waste leachate	Ava	Bloomfield	Catlin
pH	7.5	4.0	7.3	6.8
EC[b]	2.40	0.87	1.87	1.38
Ca	612	69	392	282
K	1.5	0.9	1.6	1.0
Mg	31.8	56.8	42.9	58.9
Mn	<.03	1.2	<.03	<.03
Na	192	65	106	27
SO_4	2254	305	1203	644

[a] Concentrations in mg/l

[b] millimhos/cm

solution in saturation with respect to $CaSO_4 \cdot 2H_2O$ (gypsum), which would indicate that their steady decrease in concentration through the reactor series is due to precipitation of gypsum. Due to the high ratio of leachate employed to soil moisture content, dilution is not considered to be a significant mechanism of removal.

Toxicity Studies

Ninety-six hour static bioassays were conducted with young fathead minnows (*Pimephales promelas*) to determine the toxicity of these waste leachate solutions. The toxicity tests were divided into two phases: the screening procedure and the LC-50 determination. During the screening procedure, the young fathead minnows were exposed to the full-strength leachates; in the LC-50 determinations, the minnows were exposed to full-strength leachates diluted with soft reconstituted water prepared as suggested in "Methods for Acute Toxicity Tests with Fish, Macroinvertebrates, and Amphibians" (The Committee on Methods for Toxicity Test with Aquatic Organisms, 1975). Procedures outlined in Litchfield and Wilcoxon (1949) were used for LC-50 determinations.

Ten young fathead minnows were placed into glass fingerbowls (115 x 45 mm) containing 200 ml of full-strength or diluted leachate. Each bioassay was replicated. Fish mortality data were collected at 24, 48, 72, and 96 hours after the bioassays were begun. The test organisms were not fed and the solutions were not aerated during the bioassays. Since one-half of the leachates were equilibrated under anaerobic conditions, all solutions were aerated before the fish were added. The bioassays were conducted at a constant temperature (21° ± 1°C) and with a constant photoperiod (16L-8D) in an environmental chamber. At the beginning and end of all bioassays, pH and dissolved oxygen readings were taken. Specific conductance was measured at the beginning of each bioassay.

The results of the screening procedure are depicted in Figure 4. Leachates of neutral pH (6.8 - 8.0) are relatively nontoxic. Total mortality occurs in acidic (pH <6.2) solutions.

The LC-50 values, their 95 percent confidence intervals, and dilutions necessary to eliminate mortality are listed in Table 7. The pH values listed are the pHs of full-strength leachates after they were aerated and before they were diluted with reconstituted water. There is an inverse relationship between toxicity and the LC-50 value. For example, the LC-50 values for HSR_3 and HSR_4 are 41.00 and 3.00, respectively (Table 7). Forty-one milliliters of HSR_3 diluted with 59 ml of reconstituted water is as toxic as 3.00 of HSR_4 diluted with 97 ml of reconstituted water. Thus, leachates exhibiting greater toxicity have lower LC-50 values than less toxic leachates. If, in full-strength solutions, less than 50% mortality occurred, the LC-50 is reported as greater than 100 ml/100 ml.

Generally, all leachates are acutely toxic when acidic (pH <6.2) and with increasing acidity there is an increase in toxicity and a decrease in the LC-50 value. The natural pH leachates (LSR_1, LSR_5, HSR_2, and HSR_6) are not acutely toxic and do not require a dilution to eliminate mortality (Table 7). The LC-50 values for anaerobic leachates are not significantly different from sililar aerobic solutions ($p <.05$, paired t-test).

Many factors probably contribute to the acute toxicity of the acidic leachates. It has been shown (Griffin et al., 1977)

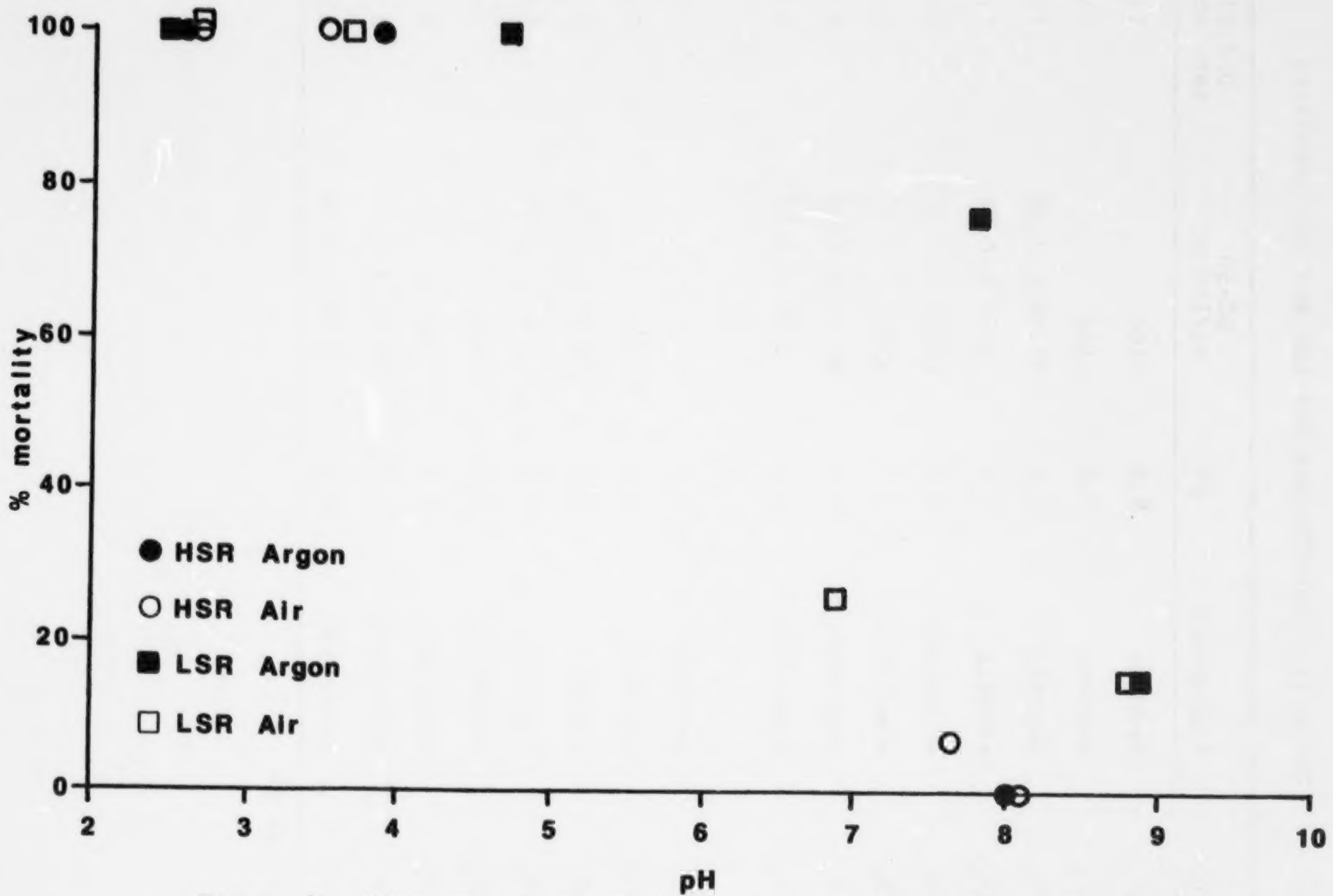


Figure 4: Plot of percent mortality vs. pH for HSR and LSR leachates.

Table 7: LC-50 Values for LSR and HSR Leachates

Sample	Atmosphere	pH	LC-50 ml/100 ml	Dilution for zero mortality
*LSR$_1$	aerobic	8.8	>100	1:1
LSR$_2$	aerobic	7.9	>100	1:1
LSR$_3$	aerobic	5.4	57.00 ± 2.28	1:3
LSR$_4$	aerobic	3.8	3.80 ± 0.41	1:50
*LSR$_5$	anaerobic	8.9	>100	1:1
LSR$_6$	anaerobic	7.7	>100	1:1
LSR$_7$	anaerobic	6.6	96.00 ± 0.83	1:1
LSR$_8$	anaerobic	4.0	2.15 ± 0.16	1:100
HSR$_1$	aerobic	8.1	>100	1:1
*HSR$_2$	aerobic	7.7	>100	1:1
HSR$_3$	aerobic	3.5	41.00 ± 2.87	1:4
HSR$_4$	aerobic	2.7	3.00 ± 0.62	1:67
HSR$_5$	anaerobic	8.0	>100	1:1
*HSR$_6$	anaerobic	8.0	>100	1:1
HSR$_7$	anaerobic	3.9	56.00 ± 2.52	1:2
HSR$_8$	anaerobic	2.6	2.30 ± 0.14	1:67

*Natural pH

that reconstituted water of low pHs (pH <5.9) will cause total mortality. Since the young fathead minnows were propagated and held at pH 7.4 and experienced a rapid change in pH, the mortality was partially due to "ionic shock." However, some acidic solutions of HSR that were neutralized by dilution were toxic. Upon neutralization, a ferric hydroxide precipitate was formed; this precipitate adhered to the mucus of the gills and resulted in suffocation. Mortality, reduced fry survival, slower growth, and reduced hatchability have been observed in other investigations of the effects of ferric hydroxide precipitates on fish (Sanborn, 1945; Sykora et al., 1972; and Smith et al., 1973).

The effects of other constituents are more difficult to assess. Although the concentrations of most of the constituents are far below LC-50 values established in previous studies for single constituents (Eaton, 1973; Pickering, 1974; and Pickering and Gast, 1973), these constituents could act synergistically and thus would contribute to the acute toxicity of the acidic leachates. The natural pH leachates are not acutely toxic; however, the chronic toxicity of these leachates has not been examined. Single constituents such as Ca, K, Pb, and Mn, which are found in relatively high but not acutely toxic concentrations in the natural pH leachates, could be chronically toxic when acting synergistically.

SUMMARY

The pollution potential from the disposal of coal cleaning wastes is of concern, if not because of the nature of the waste then because of the enormous quantity of the waste generated. In order to evaluate this pollution potential it is necessary to characterize both the solid waste and the leachate that it is capable of generating. It is then necessary to determine how the constituents can be removed from the leachate and how these constituents will effect the biota if they are not removed.

The study of two Illinois coal cleaning wastes has shown that:

1. Contamination from the wastes is most severe under acid condition.
2. Land disposal of the wastes may result in pollution by elution of contaminants from the soils themselves.
3. Toxicity to biota is not a function of acidity alone, but may also be due to the formation of precipitates during neutralization.

ACKNOWLEDGEMENTS

We gratefully acknowledge the U.S. Environmental Protection Agency, Energy Assessment and Control Division, Fuel Process Branch, Research Triangle Park, North Carolina, for partial support of this work under Contract 68-02-2130, Characterization of Coal and Coal Residue.

The authors wish to thank S. J. Russell, A. A. Debus, and the Analytical Chemistry Section of the Illinois State Geological Survey, under the direction of Dr. R. R. Ruch, for assistance in portions of this research.

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INTRODUCTION TO CHEMICAL COAL CLEANING

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INTRODUCTION

Some specific methods for the chemical removal of sulfur from coal are going to be presented in this symposium. I will attempt to present a statement of the problem associated with finding effective and economic routes to the desulfurization of coal, indicate some of the pitfalls of experimentally investigating sulfur removal in coal and present a very recent example of removal of both inorganic and organic sulfur from the same coal. I plan to emphasize the removal of organic sulfur from coal as there are now several methods for removal of pyritic sulfur, but, in my opinion, no certain method for the removal of organic sulfur has been published to date other than hydrogenation under coal liquefaction conditions.

Many of the figures will be taken from my book Coal Desulfurization, which was recently published by Marcel Dekker, Inc.(1) and the experimental examples are from our laboratories.

This presentation will consist of four sections: coal molecular structure and reactivity, sulfur removal mechanisms, criteria for economic success and an example of chemical removal of both pyritic and organic sulfur to potentially meet the revised NSPS requirements.

COAL MOLECULAR STRUCTURE

A model of the organic coal matrix, proposed by Given(2) is shown in Figure 1. Given later assessed the available knowledge on the structure of the organic sulfur units present in coal, concluding that mercaptans, sulfides, disulfides and thiophenes were the major organic sulfur containing functional groups(3). The inorganic portion of coal consists of a vast number of minerals in discrete agglomerations and often intimately associated with the organic coal matrix. The inorganic sulfur in coal occurs mainly as the mineral pyrite with small amount of inorganic sulfate minerals such as melanterite, jarosite and gypsum.

These inorganic forms can be removed either partially or totally by a number of published methods, some of which will be presented at this symposium. The removal of the organic sulfur has proved to be very difficult, as the compounds are not just intimately associated with the organic coal matrix, they are chemically bonded into the core of the carbon structure. Removal of these compounds necessarily requires a partial breakdown of the organic coal matrix.

SULFUR REMOVAL MECHANISMS

Potential methods for the removal of organic sulfur from coal have been classified into six groups as shown in Figure 2.a-c. These are: solvent partition, thermal decomposition, acid base reaction, reduction, oxidation and displacement. These mechanisms all have the common feature of being potentially capable of removing the organic sulfur content of coal as small soluble or volatile molecules, containing a prepondance of sulfur. Of these mechanisms, only reduction (with hydrogen) has been clearly shown to be effective up to the present time(4).

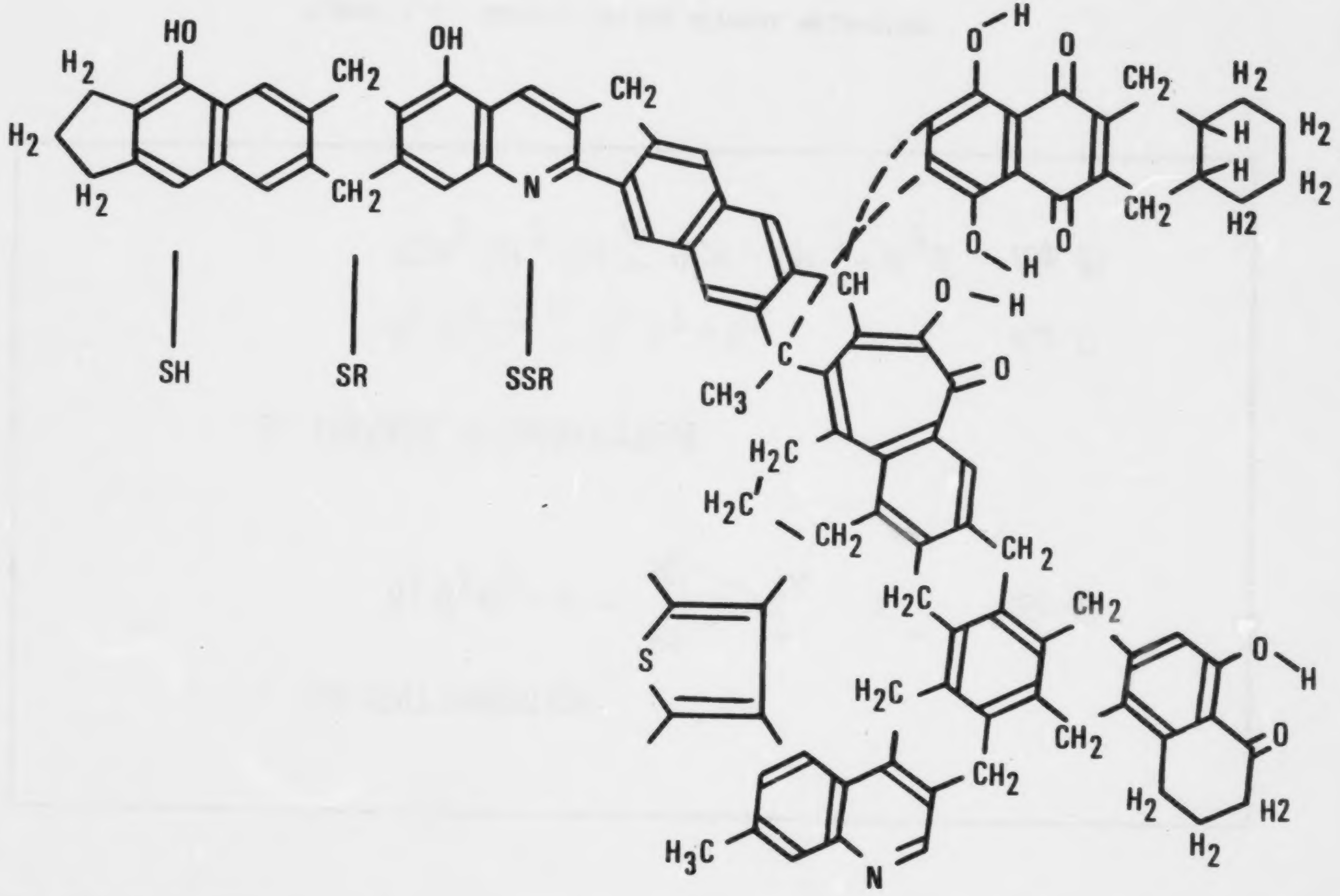
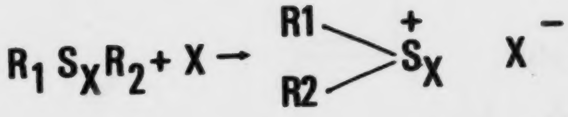


FIGURE 1. MODEL OF ORGANIC COAL MATRIX

1. SOLVENT PARTITION



$$R_1 S_X R_2 + X \rightarrow \begin{matrix} R1 \\ R2 \end{matrix} > \overset{+}{S}_X \quad X^- \qquad \textit{(Eq. 6)}$$

2. THERMAL DECOMPOSITION

$$R_1 S_X R_2 \xrightarrow[\Delta]{} R_1 R_2 + S_X \qquad \textit{(Eq. 7)}$$

$$RCH_2 CH_2 SH \xrightarrow[\Delta]{} RCH = CH_2 + H_2S \qquad \textit{(Eq. 8)}$$

FIGURE 2.a. ORGANIC SULFUR REMOVAL MECHANISMS

3. ACID-BASE NEUTRALIZATION

$$RSH + OH^- \rightarrow RS^- + H_2O \qquad \text{(Eq. 9)}$$

4. REDUCTION

$$R_1S_XR_2 + 4H \rightarrow R_1H + R_2H + H_2S_X \qquad \text{(Eq. 10)}$$

$$R_1S_XR_2 + 2R_3H_2 \rightarrow R_1H + R_2H + H_2S_X + 2R_3 \qquad \text{(Eq. 11)}$$

FIGURE 2.b. **ORGANIC SULFUR REMOVAL MECHANISMS (Continued)**

5. OXIDATION

$$R_1S_XR_2 \xrightarrow[(0)]{} R_1\,SO_3H + R_2\,SO_3\,H \xrightarrow{H_20} R_1\,OH + R_2\,OH + 2H_2\,SO_4 \qquad \text{(Eq. 12)}$$

6. NUCLEOPHILIC DISPLACEMENT

$$R_1S_XR_2 + Nu^- \rightarrow R_1S_X\,Nu + R_2^- \qquad \text{(Eq. 13)}$$

$$R_1S_XR_2 + Nu^- \rightarrow R_1S_{X-1}\,Nu + R_2S^- \qquad \text{(Eq. 14)}$$

$$R_1S_XR_2 + Nu^- \rightarrow R_1S_X^- + R_2\,Nu \qquad \text{(Eq. 15)}$$

$$R_2S^- + R_1S_{X-1}\,Nu \rightarrow R_1S_{X-1}R_2 + Nu\,S^- \qquad \text{(Eq. 16)}$$

TAKEN FROM: R. A. MEYERS, COAL DESULFURIZATION, MARCEL DEKKER, INC. (1977)

FIGURE 2.c. ORGANIC SULFUR REMOVAL MECHANISMS (Continued)

Potential pyrite removal reactions have also been categorized. These include: displacement, acid base neutralization, oxidation and reduction(1). Of these, only the displacement mechanism has not been demonstrated.

CRITERIA FOR SUCCESSFUL CHEMICAL DESULFURIZATION PROCESSES

The major criteria for economic removal of either inorganic or organic sulfur from coal are shown in Figure 3. The desulfurization reagent must be selective and not significantly react with other coal components. The reagent should be regenerable and be either soluble or volatile so it can be recovered from the coal matrix. Finally, the reagent should be inexpensive since a portion of it will certainly be lost to either irreversible sorption on the coal matrix or by reaction.

AN EXAMPLE OF REMOVAL OF BOTH PYRITIC AND ORGANIC SULFUR FROM THE SAME COAL

One of the methods discussed in Coal Desulfurization(1) was examined experimentally in our laboratories for removal of both pyritic and organic sulfur from a high sulfur coal. A well characterized sample of Kentucky No. 9 seam coal was selected for the substrate as it contained a total of 6.8 lb of $SO_2/10^6$ Btu of which half was inorganic and half organic (Figure 4 - Example 1). Treatment of this coal for 30 minutes results in removal of 38±15% of the organic sulfur and a large part of the pyritic sulfur (Example 2). However, these results were actually not particularly encouraging as the organic sulfur removal, even at "38%", is only barely significant in view of error associated with analysis. Further, the remaining total sulfur level of 2.3 lb $SO_2/10^6$ Btu is not close to meeting federal standards.

- REAGENT SELECTIVITY TOWARD SULFUR COMPOUNDS IN COAL
- REGENERATION TO THE INITIAL FORM
- SOLUBLE, VOLATILE OR OTHERWISE RECOVERABLE REAGENTS AND PRODUCTS
- INEXPENSIVE – SOME LOSS INEVITABLE

FIGURE 3. CRITERIA FOR SUCCESSFUL CHEMICAL DESULFURIZATION PROCESSES

Example	Coal	Treatment	Sulfur Content, lb/10^6 Btu				Organic Sulfur Removal
			S_T	S_p	S_s	S_o	
1	Run-of-Mine	None	6.8 ± 0.4	3.1 ± 0.2	0.6 ± 0.2	3.1 ± 0.3	
2	Run-of-Mine	Yes	2.3 ± 0.3	0.3 ± 0.2	0.1 ± 0.2	1.9 ± 0.3	38% ± 15%
3	Gravi-Float	None	3.2 ± 0.3	0.2 ± 0.2	0.3 ± 0.2	2.8 ± 0.3	
4	Gravi-Float	Yes	0.8 ± 0.4	0.2 ± 0.2	0.0 ± 0.2	0.6 ± 0.3	77% ± 17%

*30-min extraction time

FIGURE 4. ORGANIC SULFUR REMOVAL FROM KENTUCKY NO. 9 COAL*

Analysis of the coal ash indicated that there was significant reaction of the selected reagent with the mineral component of the coal. Therefore, it was decided to investigate the desulfurization reaction on "gravi-float" coal which is extremely low in ash. Gravi-float coal is obtained by float-sink separation of coal in iron sulfate leach solution at specific gravity 1.3-1.4, followed by washing with water to remove residual sulfate and additional ash. The resulting coal (Example 3) has an ash content of only 3-4%, whereas the run-of-mine Kentucky No. 9 coal has an ash content of about 12%. Further, there is essentially no pyrite in the coal. Thus, the chances for consumption of the reagent by reaction with the mineral matter is greatly reduced.

Indeed, treatment of gravi-float coal under conditions identical to those of the run-of-mine coal (Example 4) resulted in removal of $77\pm17\%$ of the organic sulfur and a total sulfur content of 0.8 lb $SO_2/10^6$ Btu. This corresponds to an overall 85% reduction in sulfur content starting with run-of-mine coal. There are a number of parameters which must be evaluated to allow economic assessment. These include: reagent loss, coal recovery, energy balance, etc. Thus, a good deal of bench-scale experimentation and engineering and economic evaluation is needed before this method can be considered for meeting New Source Performance Standards. However, the results obtained to date indicate that it may be possible to meet standards by pretreatment of coal.

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CURRENT STATUS OF CHEMICAL COAL CLEANING PROCESSES - AN OVERVIEW

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ABSTRACT

A variety of chemical coal cleaning processes are under development which will remove a majority of pyritic sulfur from coal with acceptable heating value recovery, i.e., 95 percent Btu recovery. Some of these processes are also capable of removing organic sulfur from the coal, which is not possible with physical coal cleaning methods. Chemical coal cleaning processes at the bench scale level have demonstrated removal of as much as 95 to 99 percent of pyritic sulfur and up to about 40 percent of the organic sulfur from the run-of-mine coal. It is projected that this removal efficiency could result in total sulfur reductions in U.S. coals in the range of 53 to 77 percent.

This paper presents available technical and economic information on major U.S. chemical coal cleaning processes identified during an eight-month study, conducted for the Industrial Environmental Research Laboratory of EPA at Research Triangle Park, North Carolina.

1.0 INTRODUCTION

What role should Chemical Coal Cleaning Processes play in the scenario of maximizing coal utilization without environmental deterioration? The National Energy Policy and the 1977 Clean Air Act Amendments require that more coal be burned, but with reduced sulfur emissions.

The current options for decreasing sulfur emissions from the combustion of coal are:

- pretreatment fuel processing including physical and chemical coal cleaning;
- synthetic fuels production;
- fluidized bed combustion; or
- post-combustion control technology, namely flue gas desulfurization.

Only flue gas desulfurization and physical coal cleaning are commercially available.

Physical coal cleaning can remove 60 to 90 percent of the pyritic sulfur or some 40 to 70 percent of the total sulfur in the raw coal, but cannot remove the organic sulfur. However, one problem with mechanical "deep" coal cleaning is that carbon values (BTU's) are removed with the sulfur and ash, which can result in rejecting as much as 40 percent of the total energy value of the coal.

Chemical coal cleaning processes, now being developed, remove as much as 95 percent of the mineral sulfur and up to about 40 percent of the organic sulfur. This results in removal of some 50 to 80 percent of the total sulfur in the raw coal.

Twenty-nine chemical coal cleaning processes were identified during an eight month technology overview study conducted for the Industrial Environmental Research Laboratory of EPA at Research Triangle Park, North Carolina. Eleven U.S. developed processes were classified as major processes during this study. This paper presents a summary of available technical and economic information on these processes based upon Versar's assessment, conceptual designs and costing.

2.0 SUMMARY OF TECHNICAL AND COST INFORMATION FOR MAJOR CHEMICAL COAL CLEANING PROCESSES

Table 1 shows a listing of the major processes. The first four processes listed (Magnex, Syracuse, TRW, and Ledgemont) will remove pyritic sulfur only; the remaining seven processes

TABLE 1. SUMMARY OF MAJOR CHEMICAL COAL CLEANING PROCESSES

PROCESS & SPONSOR	METHOD	TYPE SULFUR REMOVED	STAGE OF DEVELOPMENT	PROBLEMS	ANNUAL OPERATING COST $/TON CLEAN COAL INCLUDING COST OF COAL*
"MAGNEX",℠ HAZEN RESEARCH INC., GOLDEN COLORADO	DRY PULVERIZED COAL TREATED WITH FE $(CO)_5$ CAUSES PYRITE TO BECOME MAGNETIC. MAGNETIC MATERIALS REMOVED MAGNETICALLY	UP TO 90% PYRITIC	BENCH & 91 KG/DAY (200 LB/DAY) PILOT PLANT OPERATED	DISPOSAL OF S-CONTAINING SOLID RESIDUES. CONTINUOUS RECYCLE OF CO TO PRODUCE FE $(CO)_5$ REQUIRES DEMONSTRATION	40.7
"SYRACUSE" SYRACUSE RESEARCH CORP., SYRACUSE, N.Y.	COAL IS COMMINUTED BY EXPOSURE TO NH_3 VAPOR; CONVENTIONAL PHYSICAL CLEANING SEPARATES COAL/ASH	50-70% PYRITIC	BENCH SCALE	DISPOSAL OF SULFUR CONTAINING RESIDUES.	37.0
"MEYERS", TRW, INC. REDONDO BEACH, CAL.	OXIDATIVE LEACHING USING $FE_2(SO_4)_3$ + OXYGEN IN WATER	90-95% PYRITIC	8 METRIC TON/DAY PDU FOR REACTION SYSTEM. LAB OR BENCH SCALE FOR OTHER PROCESS STEPS.	DISPOSAL OF ACIDIC $FESO_4$ & $CASO_4$, SULFUR EXTRACTION STEP REQUIRES DEMONSTRATION	43.4
"LOL" KENNECOTT COPPER CO. LEDGEMONT, MASS.	OXIDATIVE LEACHING USING O_2 AND WATER @ MODERATE TEMP. AND PRESSURE	90-95% PYRITIC	BENCH SCALE	DISPOSAL OF GYPSUM SLUDGE, ACID CORROSION OF REACTORS	46.9

* RAW COAL COST IS INCLUDED AT $25/TON.

(ERDA, GE, Battelle, JPL, IGT, KVB, and ARCO) claim to remove most of the pyritic sulfur and varying amounts of organic sulfur. Also, the first two processes are unique in that the coal is chemically pretreated, then sulfur separation is subsequently achieved by mechanical or magnetic means. The remaining nine processes are more typical in that sulfur compounds in the coal are chemically attacked and converted. A capsule summary of each major process follows.

MAGNEX PROCESS

Pulverized (minus 14 mesh) coal is pretreated with iron pentacarbonyl, in this process to render the mineral components of the coal magnetic. Separation of coal from pyrite and other mineral elements is then accomplished magnetically. The process has been proven on a two hundred pound/day pilot plant scale using the carbonyl on a once-through basis. The cost of the Magnex process critically depends on the recycle of iron carbonyl. It is claimed that iron carbonyl can be produced on-site from carbon monoxide released in the process. However, the continuous recycle of carbon monoxide to produce low cost iron carbonyl requires demonstration. The use of iron carbonyl presents some difficulties from a health and safety standpoint. Approximately 40 coals, mostly of Appalachian origin, have been evaluated on a laboratory scale. For the most part, the process will produce coals which meet

TABLE 1. SUMMARY OF MAJOR CHEMICAL COAL CLEANING PROCESSES

PROCESS & SPONSOR	METHOD	TYPE SULFUR REMOVED	STAGE OF DEVELOPMENT	PROBLEMS	ANNUAL OPERATING COST $/TON CLEAN COAL INCLUDING COST OF COAL*
"ERDA" (PERC) BRUCETON, PA.	AIR OXIDATION & WATER LEACHING @ HIGH TEMPERATURE AND PRESSURE	~95% PYRITIC; UP TO 40% ORGANIC	BENCH SCALE 11 KG/DAY (25 LB/DAY) CONTINUOUS UNIT UNDER CONSTRUCTION	GYPSUM SLUDGE DISPOSAL ACID CORRROSION AT HIGH TEMPERATURES	51.6
"GE" GENERAL ELECTRIC CO., VALLEY FORGE, PA.	MICROWAVE TREATMENT OF COAL PERMEATED WITH NAOH SOLUTION CONVERTS SULFUR FORMS TO SOLUBLE SULFIDES	~75% TOTAL S	BENCH SCALE	PROCESS CONDITIONS NOT ESTABLISHED CAUSTIC REGENERATION PROCESS NOT ESTABLISHED.	41.8
"BATTELLE" LABORATORIES COLUMBUS, OHIO	MIXED ALKALI LEACHING	~95% PYRITIC; ~25-50% ORGANIC	9 KG/HR (20 LB/HR) MINI PILOT PLANT AND BENCH SCALE	CLOSED LOOP REGENERATION PROCESS UNPROVEN. RESIDUAL SODIUM IN COAL	55.9
"JPL" JET PROPULSION LABORATORY PASADENA, CAL.	CHLORINOLYSIS IN ORGANIC SOLVENT	~90% PYRITIC; UP TO 70% ORGANIC	LAB SCALE BUT PROCEEDING TO BENCH AND MINI PILOT PLANT	ENVIRONMENTAL PROBLEMS, CONVERSION OF HCL TO CL_2 NOT ESTABLISHED	46.0
"IGT" INSTITUTE OF GAS TECHNOLOGY CHICAGO, ILL.	OXIDATIVE PRETREATMENT FOLLOWED BY HYDRODESULFURIZATION AT 800°C	~95% PYRITIC; UP TO 85% ORGANIC	LAB AND BENCH	LOW BTU YIELD (<55%). CHANGE OF COAL MATRIX	55.8

*RAW COAL COST IS INCLUDED AT $25/TON.

TABLE 1. SUMMARY OF MAJOR CHEMICAL COAL CLEANING PROCESSES

PROCESS & SPONSOR	METHOD	TYPE SULFUR REMOVED	STAGE OF DEVELOPMENT	PROBLEMS	ANNUAL OPERATING COST $/TON CLEAN COAL INCLUDING COST OF COAL*
"MAGNEX", Ⓢⓜ HAZEN RESEARCH INC., GOLDEN COLORADO	DRY PULVERIZED COAL TREATED WITH FE $(CO)_5$ CAUSES PYRITE TO BECOME MAGNETIC. MAGNETIC MATERIALS REMOVED MAGNETICALLY	UP TO 90% PYRITIC	BENCH & 91 KG/HR (200 LB/HR) PILOT PLANT OPERATED	DISPOSAL OF S-CONTAINING SOLID RESIDUES. CONTINUOUS RECYCLE OF CO TO PRODUCE FE $(CO)_5$ REQUIRES DEMONSTRATION	40.7
"SYRACUSE" SYRACUSE RESEARCH CORP., SYRACUSE, N.Y.	COAL IS COMMINUTED BY EXPOSURE TO NH_3 VAPOR; CONVENTIONAL PHYSICAL CLEANING SEPARATES COAL/ASH	50-70% PYRITIC	BENCH SCALE	DISPOSAL OF SULFUR CONTAINING RESIDUES.	37.0
"MEYERS", TRW, INC. REDONDO BEACH, CAL.	OXIDATIVE LEACHING USING $FE_2(SO_4)_3$ + OXYGEN IN WATER	90-95% PYRITIC	8 METRIC TON/DAY PDU FOR REACTION SYSTEM. LAB OR BENCH SCALE FOR OTHER PROCESS STEPS.	DISPOSAL OF ACIDIC $FESO_4$ & $CASO_4$, SULFUR EXTRACTION STEP REQUIRES DEMONSTRATION	43.4
"LOL" KENNECOTT COPPER CO. LEDGEMONT, MASS.	OXIDATIVE LEACHING USING O_2 AND WATER @ MODERATE TEMP. AND PRESSURE	90-95% PYRITIC	BENCH SCALE	DISPOSAL OF GYPSUM SLUDGE, ACID CORROSION OF REACTORS	46.9

* RAW COAL COST IS INCLUDED AT $25/TON.

State regulations for sulfur dioxide emissions of 4.3 kg $SO_2/10^6$ kg cal (2.4 lb $SO_2/10^6$ BTU).

SYRACUSE PROCESS

Coal of about 3.8 cm (1½") top size is chemically comminuted by exposure to moist ammonia vapor at intermediate pressure. After removing the ammonia, conventional physical coal cleaning then effects a separation of coal from pyrite and ash. Generally, 50-70% of pyritic sulfur can be removed from Appalachian and Eastern Interior coals, producing coals which meet State regulation for sulfur dioxide emission. Construction of a 36 metric ton (40 tons per day) pilot plant is contemplated. No major technical problems are foreseen for this process other than potential problems involving scale-up to pilot plant size.

MEYERS PROCESS

The Meyers' Process, developed at TRW, is a chemical leaching process using ferric sulfate and sulfuric acid solution to remove pyritic sulfur from crushed coal. The leaching takes place at temperatures ranging from 50° to 130°C (120°-270°F); pressures from 1 to 10 atmospheres (15-150 psia) with a residence time of 1 to 16 hours. The final separation stages use an organic solvent for removal of elemental sulfur from the filtered clean coal.

The TRW Process is the only chemical coal cleaning process developed to the eight ton per day pilot scale level. The current mode of operation is a pilot scale Reactor Test Unit (RTU). Only one part of the overall system, namely the leaching-regeneration operation, has received intensive laboratory study and this is also the only process component incorporated in the RTU. The RTU came onstream in late 1977 after encountering and solving many mechanical shakedown problems. Chemical reaction data for a few 24 hour runs using minus 14 mesh coal indicate faster pyrite removal than with the bench scale reactors. Thirty-two different coals have been tested on a bench scale: twenty-three from the Appalachian Basin; six from the Interior Basin; one from Western Interior Basin and two western coals. The Meyers' Process is more applicable to coals rich in pyritic sulfur, thus it is estimated about one-third of Appalachian coal could be treated to sulfur contents of 0.6 to 0.9 percent to meet the sulfur dioxide emission requirements of current EPA NSPS. Process by-products are elemental sulfur, gypsum from waste water treatment, and a mixture of ferric and ferrous sulfate, with the latter presenting a disposal problem.

LEDGEMONT PROCESS

The Ledgemont oxygen leaching process is based on the aqueous oxidation of pyritic sulfur in coal at moderately high temperatures and pressures. The process has been shown to remove more than 90% of the pyritic sulfur in coals of widely differing ranks, including lignite, bituminous coals, and anthracite, in bench-scale tests. However, little, if any, organic sulfur is removed by the process. The process became inactive in 1975 during divestiture of Peabody Coal Company by Kennecott Copper Co. Although not as well developed as the Meyers' Process, the Ledgemont Process is judged to be competitive in cost and sulfur removal effectiveness. The principal engineering problem in this process is the presence of corrosive dilute sulfuric acid, which may pose difficulties in construction material selection and in choosing means for pressure letdown. The process also has a potential environmental problem associated with the disposal of lime-gypsum-ferric hydroxide sludge which may contain leachable heavy metals.

ERDA (PERC) PROCESS

The ERDA air and steam leaching process is similar to the Ledgemont oxygen/water process except that the process employs higher temperature and pressure to effect the removal of organic sulfur and uses air instead of oxygen. This process can remove more than 90% of the pyritic sulfur and up to 40% of the organic sulfur. The process uses minus 200 mesh coal. Coals tested on a laboratory scale include Appalachian, Eastern Interior and Western. The developer's claim is that using this process, an estimated 45 percent of the mines in the Eastern United States could produce environmentally acceptable boiler fuel in accordance with current EPA new source standards. Effort to date is on a bench scale, but a mini-pilot plant is expected to start up soon. The problems associated with this process are engineering in nature. The major one is associated with the selection of materials for the unit construction. Severe corrosion problems can be expected in this process as the process generates dilute sulfuric acid which is highly corrosive at the operating temperatures and pressures.

G.E. PROCESS

Ground coal (40 to 100 mesh) is wetted with sodium hydroxide solution and subjected to brief (∿30 sec.) irradiation with microwave energy in an inert atmosphere. After two such treatments, as much as 75-90% of the total sulfur is converted to sodium sulfide or polysulfide, which can be removed by washing. No significant coal degradation occurs. That portion of the process which recovers the sulfur values and regenerates the NaOH is conceptual. Work to date is in 100 gram quantities, but scale-up to 1 kg quantities is presently in progress. The process attacks both pyritic and organic sulfur, possibly at about the same rate. Appalachian and Eastern Interior coals having wide ranges of organic and pyritic sulfur contents have been tested with about equivalent success.

BATTELLE PROCESS

In this process, 70 percent minus 200 mesh coal is treated with aqueous sodium and calcium hydroxides at elevated temperatures and pressures, which removes nearly all pyritic sulfur and 25-50% of the organic sulfur. Test work on a bench and pre-pilot scale on Appalachian and Eastern Interior coals has resulted in products which meet current EPA NSPS for sulfur dioxide emissions. The conceptualized process, using lime-carbon dioxide regeneration of the spent leachant, removes sulfur as hydrogen sulfides which is converted to elemental sulfur using a Stretford process. In addition to being a costly process, there are two major technical problems:

- The feasibility of the closed-loop caustic regeneration feature in a continuous process is as yet undemonstrated; and
- The products may contain excessive sodium residues, causing low melting slags and making the coal unusable in conventional dry-bottom furnaces.

JPL PROCESS

This process uses chlorine gas as an oxidizing agent in a solution containing trichlorethane to convert both pyritic and organic forms of sulfur in coal to sulfuric acid. Since removal of sulfur can approach the 75% level, without significant loss of coal or energy content, products should generally meet current EPA NSPS for sulfur dioxide emissions. To date the process has been tested on a laboratory scale only, on several Eastern Interior coals. However, the effort will progress to bench-scale and pre-pilot plant scale in the near future. The project is currently supported by the Bureau of Mines. There are some potential environmental problems with the process. The trichloroethane solvent is listed by EPA as a priority pollutant in terms of environmental effects. A major cost factor is in the need to recycle by-product hydrochloric acid for conversion to chlorine. At a chlorine consumption rate of 250 kg per metric ton of coal, the incorporation of a Kel-Chlor or similar unit in the JPL system will add approximately $10/metric ton of coal.

IGT PROCESS

This process uses atmospheric pressure and high temperatures to accomplish desulfurization of coal. These high temperatures [about 400°C (750°F) for pretreatment and 815°C (1,500°F) for hydrodesulfurization] cause considerable coal loss due to oxidation, hydrocarbon volatilization and coal gasification, with subsequent loss of heating value. Experimental results have indicated an average energy recovery potential of 60% for this process. The treated product is essentially a carbon char with 80-90% of the total sulfur removed. Most of the experimental work to date has been accomplished with four selected bituminous coals with a size of plus 40 mesh. Present effort is on a bench-scale level. The net energy recovery potential of the system and the change in the coal matrix by the process have been identified as possible severe problems for the IGT Process. The process must be developed to a stage where the process off-gas can be satisfactorily utilized for its energy and hydrogen content. If this cannot be technically and economically accomplished, the process will prove to be inefficient and too costly for commercialization.

KVB PROCESS

This process is based upon selective oxidation of the sulfur constituents of the coal. Dry coarsely ground coal (plus 20 mesh) is heated in the presence of nitrogen oxide gases for the removal of a portion of the coal sulfur as gaseous sulfur dioxide. The remaining reacted, non-gaseous sulfur compounds in coal are removed by water or caustic washing. The process has progressed through laboratory scale, but is currently inactive due to lack of support. Laboratory experiments with five different bituminous coals indicate that the process has desulfurization potential of up to 63 percent of sulfur with basic dry oxidation and water washing treatment and up to 89 percent with dry oxidation followed by caustic and water washing. The washing steps also reduce the ash content of the coal.

In cases where dry oxidation alone could remove sufficient sulfur to meet the sulfur dioxide emission standards, this technology may provide a very simple and inexpensive system. Potential problem areas for this system are:

- oxygen concentration requirements in the treat gas exceed the explosion limits for coal dust, and thus the operation of this process may be hazardous.

- Nitrogen uptake by the coal structure will increase NO_x emission from combustion of the clean coal product.

ARCO PROCESS

Little information is available on this process. It is presently in the pre-pilot plant stage of development and is alleged to remove both pyritic and organic sulfur. The process was wholly funded internally until recently, when EPRI financed a study on six coals in which there was a wide distribution of pyrite particle size. Energy yield for the process is alleged to be 90-95%, and ash content can be reduced by as much as 50%.

3.0 PROCESS PERFORMANCE COMPARISONS OF SULFUR REMOVAL, HEATING VALUE RECOVERY AND COST

A comparison of process performance and costs can best be accomplished by looking at each process on a common coal feed basis. This basis allows the comparison of the following parameters process by process:

- Weight yield of clean coal product based upon a feed coal rate (moisture free basis) of 7,110 metric tons (7,840 tons) per day [7,200 metric tons (8,000 tons) per day of 2 percent moisture coal];
- Weight percent sulfur in the clean coal product based upon the sulfur removal efficiency of the process;
- Heating value yield of the process based upon a feed

coal value of 6,800 kg cal/kg (12,300 BTU/lb); and

- Costs -

  total capital costs for the process

  total annual processing costs,

  annual costs per metric ton of clean coal, including coal costs and excluding coal costs, and

  annual costs per heating value unit, including coal costs and excluding coal costs.

This comparison data is shown in Tables 2 and 3, arranged according to categories of processes.

The common coal feed selected is a bituminous coal from the Pittsburgh seam, which cannot readily be cleaned by conventional physical washing techniques to meet the current new source performance standards for sulfur dioxide emission. However, this coal does have an organic sulfur content low enough (0.7 weight percent) so that complete removal of pyritic sulfur would result in a product which will meet current NSPS for sulfur dioxide emission.

The percent removal of pyritic and organic sulfur assigned to each process is based on data supplied by individual developers. The tables indicate a range of SO_2 emission levels for the clean coal products of 1.5 to 3.8 kg/10^6 kg cal (0.8 to 2.1 lb/10^6 BTU). The calculated sulfur levels for processes which remove both types of sulfur are lower than the 2.2 kg/10^6

TABLE 2. Performance and Cost Comparison for Major Chemical Coal Cleaning Processes Which Remove Pyritic Sulfur Only.

	Feed[†]	TRW	LOL	Magnex℠	Syracuse plus physical cleaning
Net coal yield, tons/day*	7,840	7,056	7,056	6,225	6,225
Weight % sulfur in the product	1.93	0.83	0.83	0.97	1.50
Heating value, (BTU/lb)	12,300	12,835	12,835	12,400	14,600
(lb SO_2/MM BTU)	3.1	1.3	1.3	1.6	2.1
Percent net BTU yield	—	94	94	80	95
Costs					
Capital ($MM)	--	109	114.0	37.8	49.0
Annual processing ($MM)	—	37.2	45.3	19.2	12.2
$/annual ton of clean coal, excluding coal cost	--	15.6	19.1	9.2	5.8
$/annual ton of clean coal, including coal cost[Δ]	—	43.4	46.9	40.7	37.0
$/MM BTU, excluding coal cost	—	0.61	0.74	0.37	0.20
$/MM BTU, including coal cost[Δ]	—	1.69	1.82	1.64	1.27

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*All values reported are on a moisture free basis.

[†] The coal selected is a Pittsburgh seam coal from Pennsylvania which contains 1.22 weight percent pyritic, 0.01 percent sulfate and 0.70 percent organic sulfur. It is assumed that this coal has a heating value of 6,800 kgcal/kg (12,300 BTU/lb).

[Δ] Assumes coal feed @ $25/ton.

Table 3. Performance and Cost Comparison for Major Chemical Coal Cleaning Processes Which Remove Pyritic and Organic Sulfur.

	Feed†	ERDA	GE	Battelle	JPL	IGT	KVB	ARCO
Net coal yield, tons/day*	7,840	7,056	7,526	7,448	7,135	4,704	6,690	7,056
Weight % sulfur in the product	1.93	0.65	0.50	0.65	0.6	0.55	0.61	0.69
Heating value, BTU/lb	12,300	12,835	12,300	11,350	12,300	11,685	13,120	12,400
lb SO_2/MM BTU	3.1	0.9	0.8	1.2	1.0	0.9	0.9	1.1
Percent net BTU yield	—	94	96	88	91	57	91	91
Costs								
Capital ($MM)	—	166.8	102.0	168.6	103.2	134.6	65.9	—
Annual processing ($MM)	—	56.6	39.8	74.2	44.4	38.3	41.0	58.7
$/annual ton of clean coal, excluding coal cost	—	23.8	15.7	29.6	18.5	24.2	18.2	25
$/annual ton of clean coal, including coal cost$^{\Delta}$	—	51.6	41.8	55.9	46.0	65.8	47.5	—
$/MM BTU, excluding coal cost	—	0.92	0.64	1.30	0.75	1.03	0.69	—
$/MM BTU, including coal cost$^{\Delta}$	—	2.00	1.69	2.45	1.86	2.81	1.81	—

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* All values reported are on a moisture free basis.

† The coal selected is a Pittsburgh seam coal from Pennsylvania which contains 1.22 weight percent pyritic, 0.01 percent sulfate and 0.70 percent organic sulfur. It is assumed that this coal has a heating value of 6,800 kgcal/kg (12,300 BTU/lb).

Δ Assumes coal feed @ $25/ton.

kg cal (1.2 lb/10^6 BTU) current NSPS for sulfur dioxide emission. Of the four processes which remove pyritic sulfur only, two (TRW and Ledgemont) will produce slightly higher sulfur levels than that required to meet the current NSPS; however, within the levels of accuracies involved they also might be considered to be in compliance. The remaining two processes [Magnex℠ and Syracuse] would produce coal which would be in compliance only with a standard of 4.3 kg/10^6 kg cal (2.4 lb/10^6 BTU) for sulfur dioxide emission.

The heating value yields estimated for these processes are generally greater than 90 percent, with a range from a low 57 percent for the IGT Process to a high of 96 percent for the GE Process. All heating value yields reflect both the coal loss due to processing and the coal used to provide in-process heating needs. However, with the exception of the IGT Process, the actual coal loss due to processing is claimed to be small. For most processes, the major heating value loss is due to the use of clean coal for in-process heating.

It is believed that the high yield estimated for the GE Process may not adequately reflect the heat requirements that may be needed to regenerate the caustic reagent used in the process. This process is in its early stage of development and as such, the energy requirements for the process cannot be properly assessed at this time. It is possible, that in the final analysis, the heating value recovery from this process will be more in line with other chemical coal cleaning processes.

COST COMPARISON

Estimates of capital and annual operating costs for each major chemical coal cleaning process are presented in Tables 2 and 3. These estimates are based on an assumed plant throughput capacity of 7,200 metric tons (8,000 tons) per day, equivalent to a 750 M.W. utility boiler. The total annual operating costs for each process, including and excluding cost of the raw coal, have been expressed also in terms of dollars per ton and dollars per million BTU heat content in the coal.

The capital cost estimate prepared by each process developer was used as the basis of the cost estimates in this report. In some cases, these costs were modified to allow the evaluation of the various processes on a comparable basis. The estimate capital costs assume a grass roots operation including costs for coal crushing, grinding, product compacting and feed and product handling. The capital costs also include land acquisition and site development, off-site facilities, and engineering and design costs. A contingency allowance of 20 percent has been included in all estimates, with the exception of TRW's. A lower contingency allowance (10 percent) was used for the TRW process since it is at a more advanced stage of development and adequate process data is available to develop the economics of this process with a greater degree of confidence.

Annual operating costs are based on a 24-hour workday, 90.4 percent service factor (330 days per year) basis. The capital cost is amortized over a period of 20 years at 10 percent interest per year. Where adequate information was available, the utilities and chemical consumptions are based upon actual process demand. The operating labor costs reflect wage rates for the Pittsburgh, Pennsylvania, area. The estimates for the maintenance and supplies, general and administrative, taxes and insurance are taken as 5, 1.5, 2 and 1 percent on total installed plant capital cost (TPC), respectively.

CAPITAL COST COMPARISONS

In general, pyritic sulfur removal processes require the least amount of capital investment. However, these processes have limited sulfur removal efficiencies.

Among processes that remove both organic and pyritic sulfur, the KVB Process appears to have the lowest capital investment, since it is a partially dry process requiring lower investment for the dry reaction section. The high capital cost of the Battelle Process is due to the processing steps associated with reagent regeneration.

The high capital cost of the ERDA Process is due to costly equipment associated with the handling of dilute sulfuric acid at elevated temperatures and pressures. At the process operating conditions the dilute acid is highly corrosive and it poses problems in terms of selection of construction material for equipment and devices which are exposed to the corrosive atmosphere.

Very little is known about the ARCO Process details and process chemistry. Therefore, a capital cost estimate was not developed for that process.

OPERATING COST COMPARISONS

The ranges of annual operating costs, including raw coal cost, in terms of \$/ton and \$/10^6 BTU are \$37.00 to \$65.00 and \$1.27 to \$2.81, respectively. Pyritic sulfur removal processes using chemical pretreatment are the least expensive of all processes studied. Operating cost for the Magnex process depends primarily on the cost of iron pentacarbonyl manufacturing. In the estimate presented in Table 2, an operating cost of \$0.22/kg for the iron carbonyl manufacturing was used, as projected by the developer. At a consumption rate of 10 kg/metric ton of coal, each \$0.20 cost increase per kilogram of iron carbonyl manufactured would increase the annual operating cost of this process by about 27 percent.

Between the two processes which remove pyritic sulfur by leaching, the TRW Process appears to be slightly less costly. In the Ledgemont Process the fixed charges associated with the higher capital investment have an adverse impact on the annual operating costs. Additionally, the TRW Process has a higher probability of technical success, since it is currently active at a PDU stage. The Ledgemont Process, tested only at a mini-pilot plant level, is currently inactive.

The most expensive processes, in terms of energy output, are the IGT process followed closely by the Battelle Process. Laboratory data available at this time, indicate a very low BTU recovery for the IGT Process. The Battelle Process is adversely impacted by the fixed charges associated with the high capital investment and by the costs associated with chemicals consumption and reagent regeneration operations.

The least expensive process capable of removing pyritic and organic sulfur is the GE Process followed closely by the JPL and KVB Processes. The GE estimate is based, however, on early laboratory data and it is quite possible that the projected costs will prove somewhat inaccurate in the long run. The basic process utilizes a caustic reagent in coal pretreatment and the costs associated with caustic consumption and caustic regeneration are questionable at this time. The JPL Process estimates are also preliminary since investigations on this process are at an early stage. The annual costs reported for the KVB Process are also preliminary since the process is at its early stages of development and accurate conceptualization of the process for purposes of economic evaluation is difficult. The main advantage of the KVB Process is the simplicity of the first stage dry oxidation process. If the dry oxidation process can be successfully demonstrated using coarse coals, this process would be an inexpensive technology for beneficiation of coals where partial removal of sulfur would substantially upgrade the coal.

Among the processes capable of removing pyritic and organic sulfur the ERDA Process has one of the highest probabilities of technical success. The process is currently active and most technologies employed in this system have been already tested in other systems such as Ledgemont and TRW. The process is attractive because it is claimed to remove both types of sulfur and uses air as a major reagent. Furthermore, the sulfur by-product from this process is a dilute sulfuric acid, rather than iron sulfate, which greatly simplifies the coal washing operations. The process is somewhat expensive due to high operating temperature and pressure requirements and the corrosive nature of dilute acid present in this system. The dilute sulfuric acid at the operating conditions of the ERDA Process will require the use of expensive construction material and consequently a higher capital investment cost.

Table 4 presents a cost effectiveness summary derived from information presented in Tables 2 and 3. Costs are presented in terms of dollars per percent of sulfur removed from coal

TABLE 4. COST EFFECTIVENESS COMPARISON OF CHEMICAL COAL CLEANING PROCESSES*

Process	Type of Sulfur Removed	Sulfur Removed (Wt.%)*	Process Cost ($/ metric ton incl. cost of coal)	Cost Effectiveness of S removal, $/% S removed	Cost Effectiveness Ranking	Meets EPA NSPS*	Probability of Success (based on available info.)	Time Frame for Commercial Availability (Years)$^{\alpha}$
Magnex	P$^{\Delta}$	0.96	44.8	46.6	2	No	85%	2-3
Syracuse & Physical Cleaning	P	0.43$^{\beta}$	40.8	94.9	4	No	70%	2-3
TRW	P	1.10	47.9	43.5	1	No	90%	<3
LOL	P	1.10	51.6	46.9	3	No	50%$^{\partial}$	4-5
ERDA	(P&O)†	1.28	56.9	44.5	4	Yes	70%	5
GE	(P&O)	1.43	46.0	32.2	1	Yes	60%	5
Battelle	(P&O)	1.28	61.6	48.1	5	Yes	35%	4-5
JPL	(P&O)	1.33	50.7	38.1	2	Yes	55%	5
IGT	(P&O)	1.38	72.6	52.6	6	Yes	20%$^{\partial}$	5
KVB	(P&O)	1.25	52.4	41.9	3	Yes	20%$^{\partial}$	5
ARCO	(P&O)	1.24	-$^{\Lambda}$	-$^{\Lambda}$	-	Yes	-$^{\Lambda}$	-$^{\Lambda}$

NOTES:

* Based on Pittsburgh seam coal from Pennsylvania which contains 1.22 weight percent pyritic, 0.01 percent sulfate and 0.70 percent organic sulfur.

Δ P = pyritic sulfur.

$\dagger$ (P&O) = pyritic and organic sulfur.

α Time frame assumes continuing effort or renewed effort starting immediately.

Λ Information available is insufficient to make educated guesses.

∂ Process not currently active, partially accounting for low probability of success.

β 80 percent yield of product assumed in cleaning plant.

regardless of the quality of the treated product. The processes are then rated based upon the cost effectiveness of sulfur removal. The subjective probability of success assigned to each process is based on integration of several factors such as:

- available experimental data;
- our understanding of the status of the process;
- known product quality deficiencies;
- known process problems; and
- the degree and quality of effort assigned to the individual program.

In conclusion, all chemical coal cleaning processes discussed in this section offer a possibility of converting coal into clean fuel. Each process has an area of application. However, processes that remove both pyritic and organic sulfur are judged to have a greater impact in future coal utilization.

STATUS OF THE REACTOR TEST PROJECT FOR CHEMICAL REMOVAL OF PYRITIC SULFUR FROM COAL

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ABSTRACT

Plant checkout and shakedown was completed at the end of September and initial plant process performance was evaluated on an Appalachian coal. Operation of the plant through January of 1978 demonstrated that the Reactor Test Unit (RTU) could be run continuously in three-shift operation to reduce the coal from 2.4 lbs $SO_2/10^6$ Btu to a level of 1.0 to 1.2 lbs $SO_2/10^6$ Btu, after rinsing and extraction of generated elemental sulfur. There was no measurable coal oxidation during processing and leach rates in the plant were greatly improved over bench-scale values. The leach solution/coal/oxygen environment was found to be corrosive to the installed stainless steel reactor, necessitating future upgrading to support additional testing. Bench-scale experimentation showed that the leach solution can be used as a homogeneous dense-media to efficiently gravity-separate coal prior to processing. Beneficial engineering cost improvements are obtained based on using this approach, resulting in capital cost estimates of \$68-\$69/KW and with \$0.44-\$0.50/10^6 Btu processing costs, including amortization of capital, for input coal costing \$0.78-\$0.81/10^6 Btu. Overall energy efficiency was 93 to 96 percent.

INTRODUCTION

The Meyers Process is a technology for chemically removing essentially all of the pyritic sulfur from coal through a mild oxidative treatment. Important pollutant trace elements, lead, cadmium and arsenic, are removed at the same time. It can be used to provide compliance coal for industrial boilers and smaller electric utilities, and for recovery and desulfurizing waste fine coal rejected from mining and washing operations. The development of the process is sponsored by the U.S. Government's Environmental Control Technology Program administered by the Environmental Protection Agency.

A process schematic is shown in Figure 1. Coal is mixed with an aqueous solution of ferric sulfate (Step 1), previously derived from the coal, to form a slurry. The slurry is raised in temperature to 100-130°C (Step 2) where the ferric sulfate oxidizes the pyritic sulfur content of the coal to form elemental sulfur and additional iron sulfate. At the same time oxygen or air is introduced to the wet slurry mix to regenerate the reacted ferric

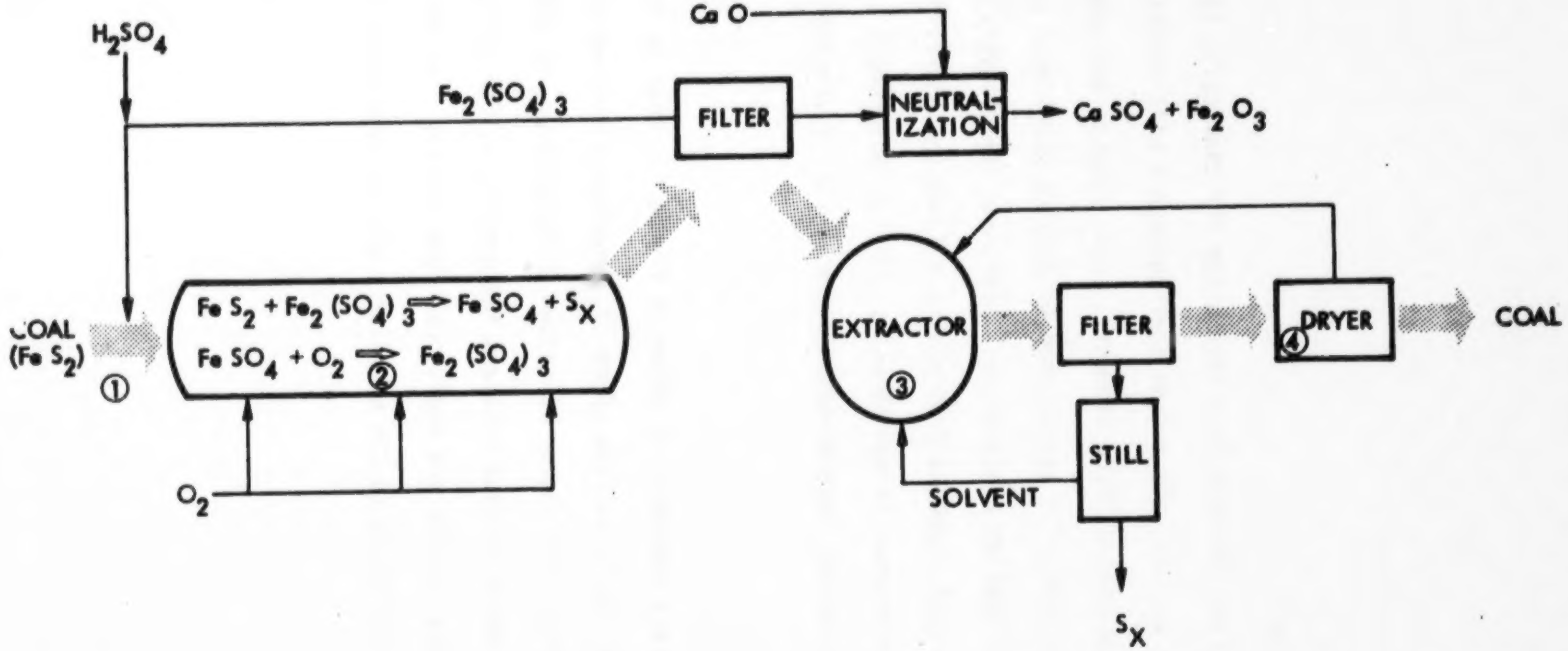

Figure 1. Meyers Process

sulfate. Iron sulfate dissolves into the leach solution while the elemental sulfur is solvent-removed in a second extraction (Step 3). The coal is dried and solvent recovered (Step 4). The products of the process are iron sulfate, which may be limed to give a dry gypsum and iron oxide material, and elemental sulfur. Trace elements from the coal are bound in with the stabilized gypsum/iron oxide solid.

Elemental sulfur is the most desirable product which can be obtained in the process of controlling sulfur oxide pollution, and be easily stored without secondary pollution or may be marketed. The gypsum/iron oxide is a safe and storable solid.

Very recent operating experience has demonstrated that the iron sulfate/sulfuric acid leach solution can be used as a homogeneous dense media to efficiently gravity-separate fine coal at specific gravities of 1.2-1.35. Beneficial engineering cost improvements are obtained using this gravity-separation technology. A significant portion of the input coal, which characteristically floats in the leach solution and is almost pyrite free, may bypass the reactor, elemental sulfur extraction and dryer portions of the Meyers Process (Figure 2). This revised technology is termed the Gravichem Process. For example, when applied at bench-scale to a Tennessee Valley Authority (Interior Basin) coal containing 12% ash and 7 lb $SO_2/10^6$ Btu, two products are obtained in roughly equal amounts, a 4% ash float coal containing 3 lb $SO_2/10^6$ Btu, and an 11-12% ash sink coal containing 4 lb $SO_2/10^6$ Btu after treatment by the Meyers Process. Both of these products meet state SO_x emission standards for utility systems using this coal. Because of these promising results, TVA has shipped 300 tons of coal to TRW

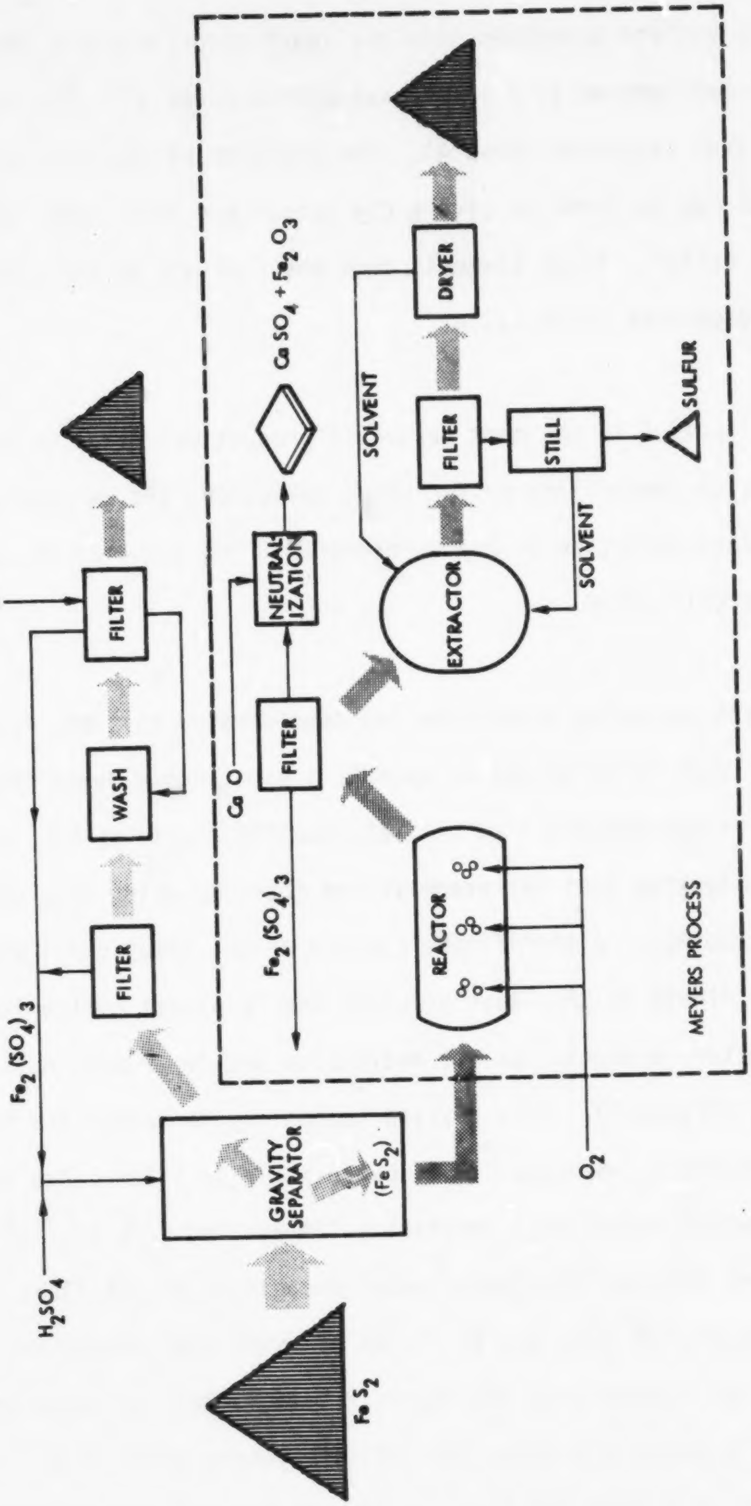

Figure 2. Gravichem Process

for future processing and evaluation. A description of the test plant, operational results and process sulfur emissions reduction potential is presented in the sections to follow.

THE TEST PLANT

After testing the process at bench-scale on some 40 U.S. coals (Meyers, 1977; Hamersma and Kraft, 1975; Hamersma, et al., 1973) and performing 200 fully material-balanced bench-scale extractions (Hamersma, et al., 1973; Koutsoukos et al., 1976), the value of the process for controlling the sulfur content of coal was firmly established. Additionally, the data necessary for the design of a test plant was then available. Engineering design criteria obtained through extensive studies at TRW (Hamersma et al., 1973; Koutsoukos et al., 1976; Van Nice and Santy, 1977) and various other engineering organizations (Nekervis and Hensley, 1975; McGee, 1975) provided confidence that the process was economically attractive and identified important engineering data which could only be obtained by operation of a pilot-plant test facility.

It was determined that the initial test facility process evaluation should concentrate on the key process steps of coal/leach solution slurry formation, leaching, regeneration and filtration. A test plant, termed the Reactor Test Unit (RTU), was constructed at TRW's San Juan Capistrano site for the purpose of testing these portions of the process (Figure 3). The plant, sized to process from 1/8 to 1/3 ton/hour of coal, was dedicated in April 1977.

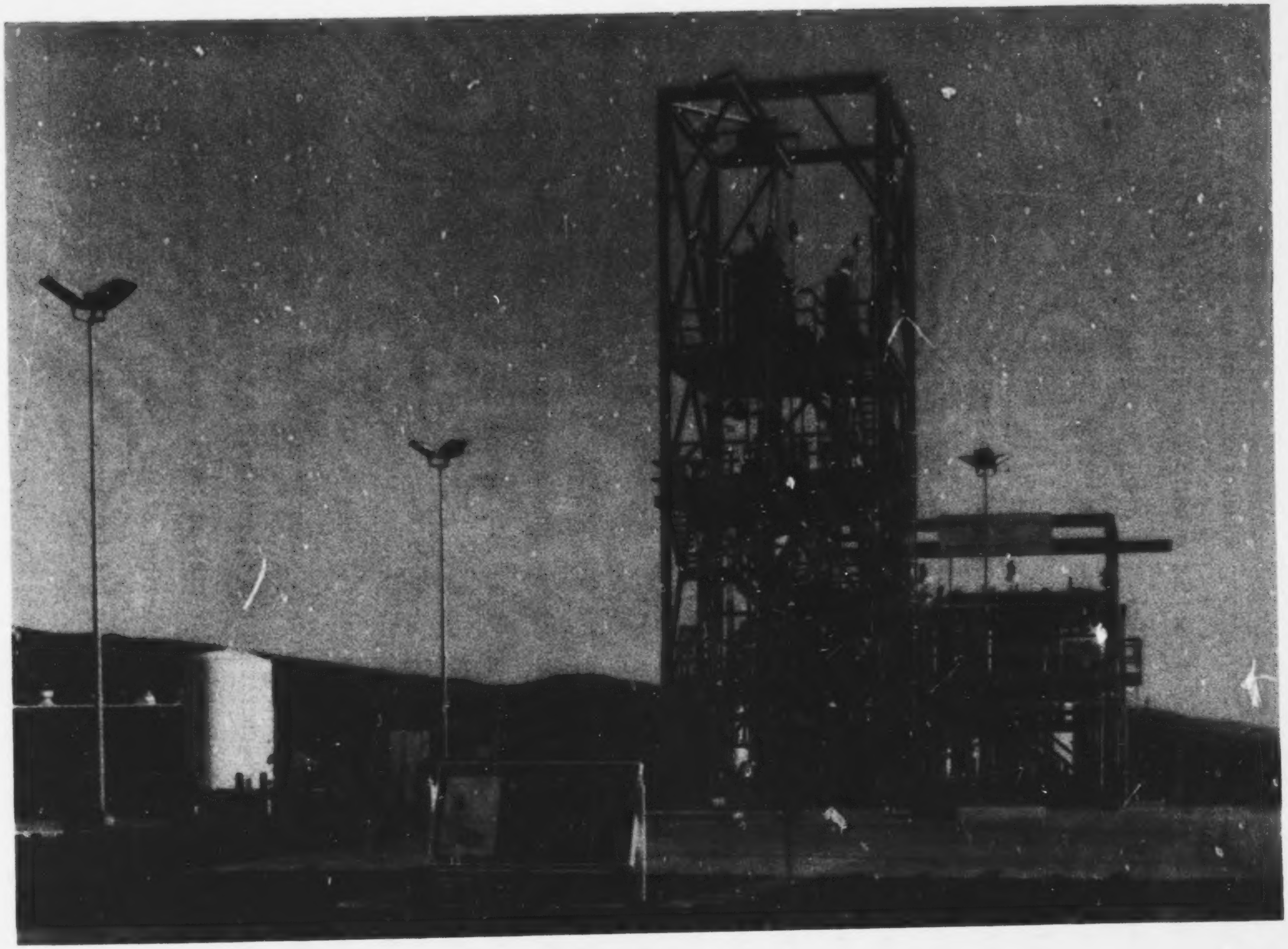

Figure 3. Reactor Test Unit

The facility was designed to demonstrate those unit operations comprising the front end of the Meyers Process, namely, coal/reagent mixing, primary pyrite reaction and reagent regeneration, secondary (finishing) pyrite reaction and slurry filtration. Designed for high flexibility, the RTU has the capability of processing a range of suspendable coals up to approximately 8 mesh top-size and coarse coals up to approximately 3/8-inch top-size. Spent reagent may be regenerated either exclusive of, or simultaneously with, coal leaching. The primary reactor may be used as either a five-stage or a three-stage reaction unit to increase the available range of coal processing times.

A process flow diagram of the RTU is shown schematically in Figure 4. Fine coal ground to the desired size is loaded in feed tank T-1. Dry coal is fed continuously by live bottom feeder A-2 to weigh belt A-3 which discharges through rotary valve A-4 to three-stage mixer T-2 (stream 1). Aqueous iron sulfate leach solution (stream 2) enters T-2 after preheating in heat exchanger E-2 and passing through foam scrubber T-3. Steam is added (stream 3) to raise the slurry to its boiling point. Foaming, which may occur during the early stages of mixing, ceases when coal particle wetting is complete. The heated slurry (stream 4) is then pumped to five-stage pressure vessel R-1 in which most of the pyrite is removed. R-1 slurry heating is achieved by direct injection of steam into any or all reaction stages. Reagent regeneration may be carried out simultaneously with pyrite leaching by means of oxygen injection into any or all reaction stages (stream 5). Unused oxygen saturated with steam (stream 6) is contacted in foam knockout drum V-1 with the feed reagent (stream 7) to preheat the reagent and cool vent gases. Slurry in any stage of R-1 may be

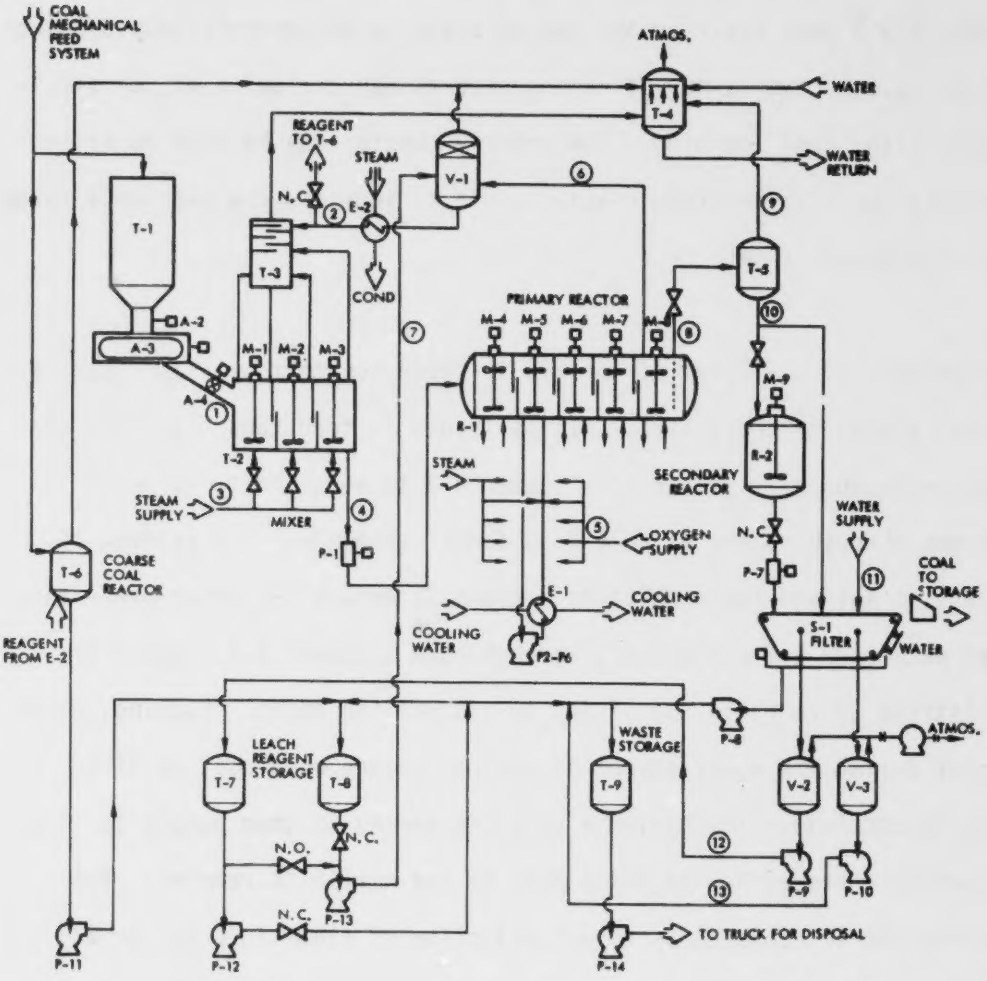

Figure 4. RTU schematic

cooled by means of cooling water heat exchanger E-1 which may be applied to slurry recirculation loops for removal of excess heat of reaction. Vent gas from both T-3 and V-1 are water scrubbed in T-4 to remove any traces of acid mist.

Reacted coal slurry (stream 8), at elevated temperature and pressure, is flashed into flash drum T-5 for gas/liquid separation. Generated steam (stream 9) is condensed in T-4, and the condensate plus any entrained acid mist is removed with scrubber water. Reacted slurry (stream 10) is fed to belt filter S-1. The filtrate, which is regenerated leach solution, is removed from the coal slurry through evacuated filtrate receiver V-2 and pumped (stream 12) to leach solution storage tank T-7. Coal on the filter belt (Figure 5) is washed with water (stream 11) and discharged to coal storage. Wash water is removed through evacuated wash water receiver V-3 and pumped (stream 13) to liquid waste holding tank T-9 for subsequent disposal.

As a processing alternate, partially processed slurry from T-5 may be loaded into secondary reactor R-2 for final depyritization in a batch mode. Slurry may be retained, heated and agitated for extended periods of time in R-2 prior to being pumped to S-1.

Coarse coal contacting vessel T-6 is a steam heated insulated tank in which hot reagent may flow through a bed of retained coarse coal. This unit is used principally to convert regenerated leach solution in storage tank T-7 or T-8 to a more depleted solution simulating recycle reagent after secondary reaction. T-6 is basically a coarse coal reactor and, if appropriate sampling ports and possibly some flow distribution internals were added, could be used to obtain design data for coarse coal processing.

PLANT OPERATION AND PROJECT RESULTS

Plant checkout and shakedown was completed at the end of September 1977 and initial plant process performance was evaluated on coal donated by the American Electric Power Service Corporation (AEP) from its Martinka mine in West Virginia (Hart et al., 1978). Operation of the plant, through January of 1978, demonstrated that the RTU could be run continuously in three-shift operation to reduce the AEP coal from 2.8 lb $SO_2/10^6$ Btu to a level of 1.0-1.2 lb $SO_2/10^6$ Btu, following rinsing and extraction of generated elemental sulfur (Table 1). Thus, the process coal meets New Source Performance Standards of 1.2 lb $SO_2/10^6$ Btu. The coal product is shown as a cake on the plant filter belt in Figure 5. There was no measurable coal oxidation; in fact, heat content increases averaged 350 Btu/lb due to pyrite and ash removal. Leach rates in the RTU were greatly improved over bench-scale values, thus enabling bypass of the secondary reactor.

To fully appreciate the apparent leach reaction rate increase, data obtained from the RTU acidified iron reagent operations is correlated with the previously established (at bench-scale) pyrite leaching rate expression, namely:

$$r_L = \frac{-dW_p}{dt} = K_L W_p^2 Y^2 \qquad (1)$$

where

r_L is the pyrite leaching rate, expressed in weight of pyrite removed per 100 weights of coal per hour (rate of coal pyrite concentration reduction),

Run	Reactor Temp. °F	Coal Analysis		Sulfur % w/w	$\frac{\text{lb } SO_2}{10^6 \text{ Btu}}$
		Ash % w/w	Heat Content, Btu/lb		
Starting Coal	-	16.11 ±0.261	12508 ± 77	1.73 ±0.045	2.8
1	222	12.97 ±0.0894	13258 ± 162	0.68 ±0.044	1.03
2	232	12.02 ±0.636	13388 ± 91	0.78 ±0.065	1.17
3	234	12.51 ±0.953	13265 ± 155	0.75 ±0.033	1.13

Table 1. Test plant data taken over 5-day period

Figure 5. Desulfurized coal on filter belt

W_p	is the pyrite concentration in coal at time t in wt. percent,
t	is the reaction (leaching) time in hours,
K_L	is the pyrite leaching rate constant (a function of temperature and coal particle size) expressed in $(\text{hours})^{-1}$ $(\text{wt. percent pyrite in coal})^{-1}$,
Y	is the ferric-iron-to-total-iron ratio in the leacher at time t, dimensionless, and

with

$$K_L = A_L \exp(-E_L/RT) \tag{2}$$

where

A_L is the Arrhenius frequency factor in the units of K_L,

E_L is the apparent activation energy in calories/mole,

R is the gas constant in calories/mole °K, and

T is the absolute temperature, in °K.

This rate expression was used in conjunction with a model of the reaction system as a series of continuous-flow stirred-tank reactors. Measured slurry temperatures and reagent Y values for each reaction stage were input for each experimental condition and the value of K_L was determined at the various reaction temperatures tested.

Equation (2) indicates that a plot of $\ln K_L$ vs. $1/T$ should yield a straight line having a slope of $-E_L/R$ and an intercept of $\ln A_L$. An Arrhenius plot of the data from several experiments is presented in Figure 6. A very good linear correlation was obtained. The apparent activation energy and frequency factor indicated by these data are:

$E_L = 26.9 \times 10^3$ calories/mole, and

$A_L = 9.2 \times 10^{14}\ W_p^{-1}\ hr^{-1}$

These values may be compared with bench-scale coal processing results which yielded an E_L (bench) of 11.1×10^3 calories/mole and A_L (bench) of $2.95 \times 10^5\ W_p^{-1}\ hr^{-1}$. Hence, K_L (RTU) was measured to be 3 to 8 times greater than K_L (bench) for 14 mesh top-size coal at temperatures between

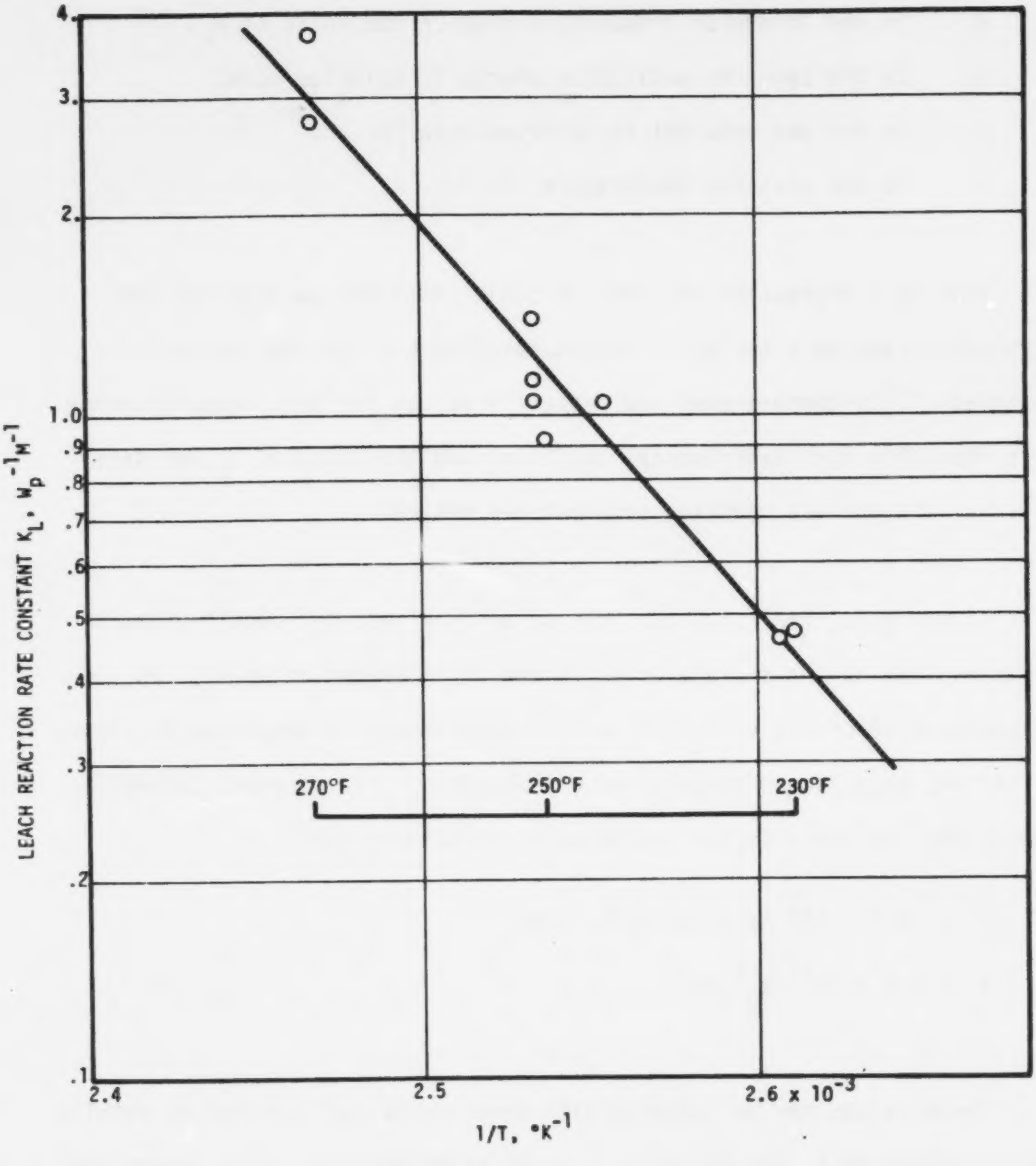

Figure 6. Arrhenius plot of data obtained during RTU processing

230°F and 270°F. The deviations of A_L and E_L from the values obtained during batch reactor (bench scale) operation were only partially anticipated. The apparent value of A_L was expected to increase during stagewise operation as the mixing in reaction stages deviated from ideal and the average particle residence time per stage increased. Also, under non-ideal mixing, pyrite rich particles might be expected to have longer residence times than pyrite lean particles which have a lower density. Thus, coal processing in a continuous flow stirred tank reactor is expected to result in a higher apparent A_L value than would identical coal processing in a batch reactor. However, the apparent doubling of the activation energy E_L above E_L (bench) was not anticipated. To effect such an increase in E_L requires that deviations from ideal mixing or segregation of pyrite rich coal particles increase with increasing temperature. A decrease in reagent density could increase coal segregation despite mechanical mixing and, perhaps, selectively cause the pyrite rich coal particles to remain longer in each reaction stage. While density changes due to temperature alone are small, this effect coupled with reagent dilution (due to direct steam heating in the RTU) can be significant. The combined temperature and steam dilution effects are estimated to have resulted in mean reagent densities of 1.15 g/cc during 230°F tests, 1.08 g/cc during 250°F tests and 1.06 g/cc during 270°F tests. Thus, significant reagent density differences occurred between the 230°F and 270°F experimentation which may have resulted in the apparent increase in the pyrite leaching activation energy. Whether or not this density difference is in itself sufficient to cause the observed factor of 2 increase in activation energy cannot be determined from available data. However, if part of the observed increase is the result of a density effect then reagent density would become an important reaction design parameter for systems utilizing stirred tank reactors. Changes in viscosity and slurry concentration may also be important.

As is the case with most new process pilot-plant-scale startups, numerous equipment and materials problems were encountered during operation. The more severe problems resulted in significant plant downtime. These problems included: filter belt (S-1) misalignment and hangup, errors in weigh belt (A-3) calibration, slurry feed pump (P-1) malfunction, and corrosion in primary reactor (R-1) and its associated pump-around loops. All of these equipment problems were identified and solved during the operational phase of the project. It is important to note that, in general, none of the problem areas encountered during RTU operation were process oriented but rather pilot-scale equipment related.

During the first 2 months of operation, RTU vacuum filter belt (S-1) experienced numerous shear pin failures. These failures usually occurred several hours into experimental runs and resulted in premature run termination. The problem was originally believed to be one of improper belt alignment resulting in excessive power train exertion. However, following several belt alignments and power train adjustments, which did not solve the shear pin failure problem, it was further determined that excessive frictional forces were being experienced at the rubber-drive-belt/vacuum-pan interface. These forces were sufficiently strong to result in one instance of drive belt separation (Figure 7). The problem was resolved by attaching Teflon skids to the vacuum pans at the rubber belt interface.

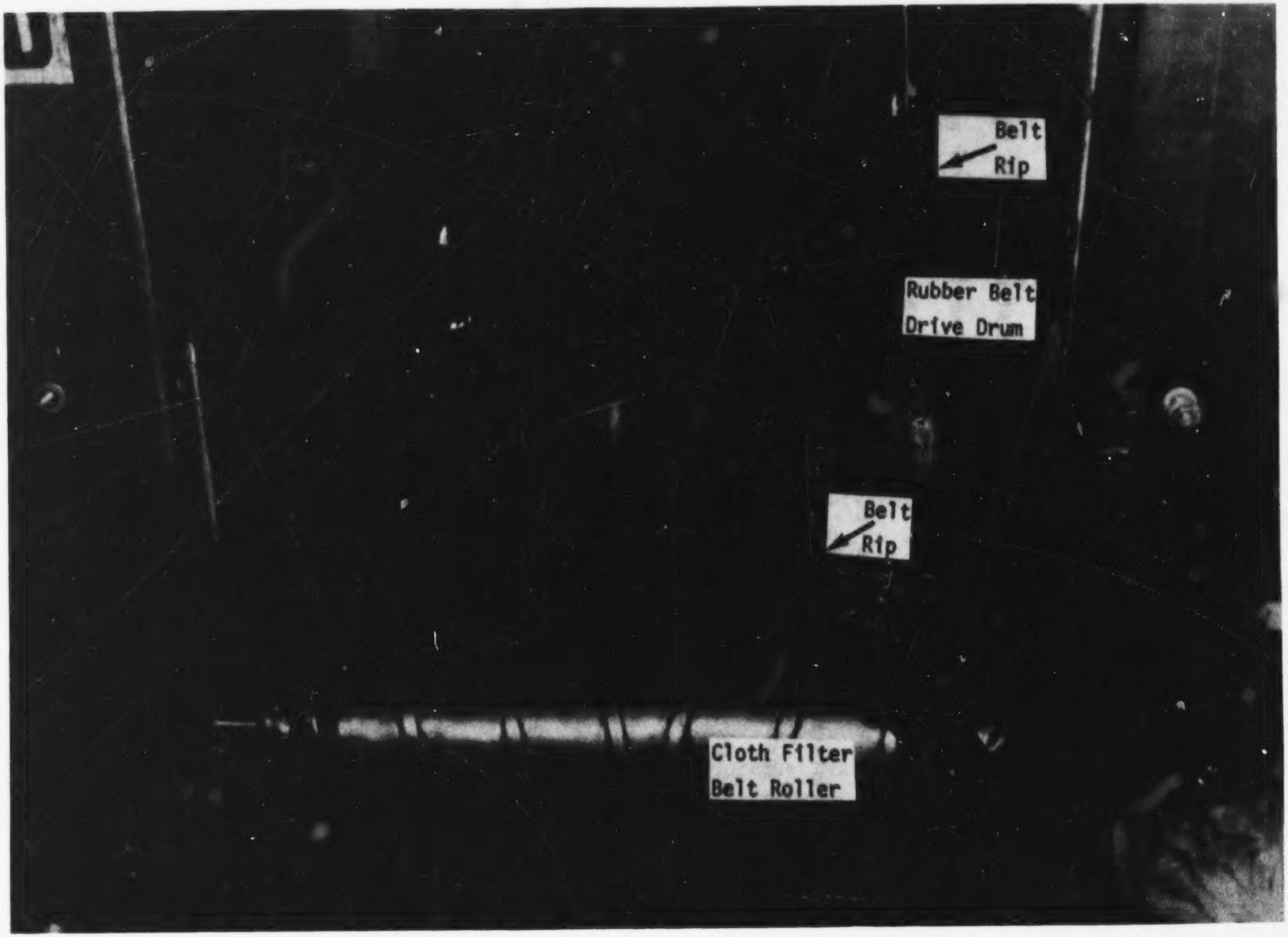

Figure 7. Ripped S-1 filter belt (cloth belt removed)

The belt was repaired, reassembled and placed back into service with no further shear pin failures or belt tears experienced.

During the initial phases of shakedown operations, RTU weigh belt coal feeder (A-3) was found to be overly temperature sensitive and unable to operate to the specified calibration limits. Most of the belt internals, including mechanical and electric components, were modified and/or replaced by the manufacturer during several cycles of rework at both the Capistrano Test Site and the manufacturer's facility. The modified unit which is currently installed in the RTU has repeatedly demonstrated its ability to achieve the desired accuracy range of ±1 percent over the approximate 100 to 1000 pound per hour delivery range.

Another recurring problem experienced during RTU operations was that of slurry feed pump (P-1) failure. Feed pump (P-1) and its replacement spare are six-stage progressive cavity type pumps. The pump failures were manifested as gradual losses of pumping capability at constant head pressures. It was determined upon inspection of pump internals that the chrome plated 316 stainless steel rotors were experiencing rapid corrosion and/or erosion (Figure 8). Subsequent material evaluations and discussions with the pump supplier indicated that the pumps were inadvertently incorrectly specified and that the units should have been supplied with Hastelloy-C rotors. Due to the relatively long delivery time (several months) for obtaining replacement Hastelloy-C rotors, efforts were made to resurface and rechrome the existing rotors and to operate the RTU while awaiting delivery of the replacement rotors. The reworked 316 stainless steel rotors were found to operate successfully for times ranging from 1/2 hour to 100 hours depending

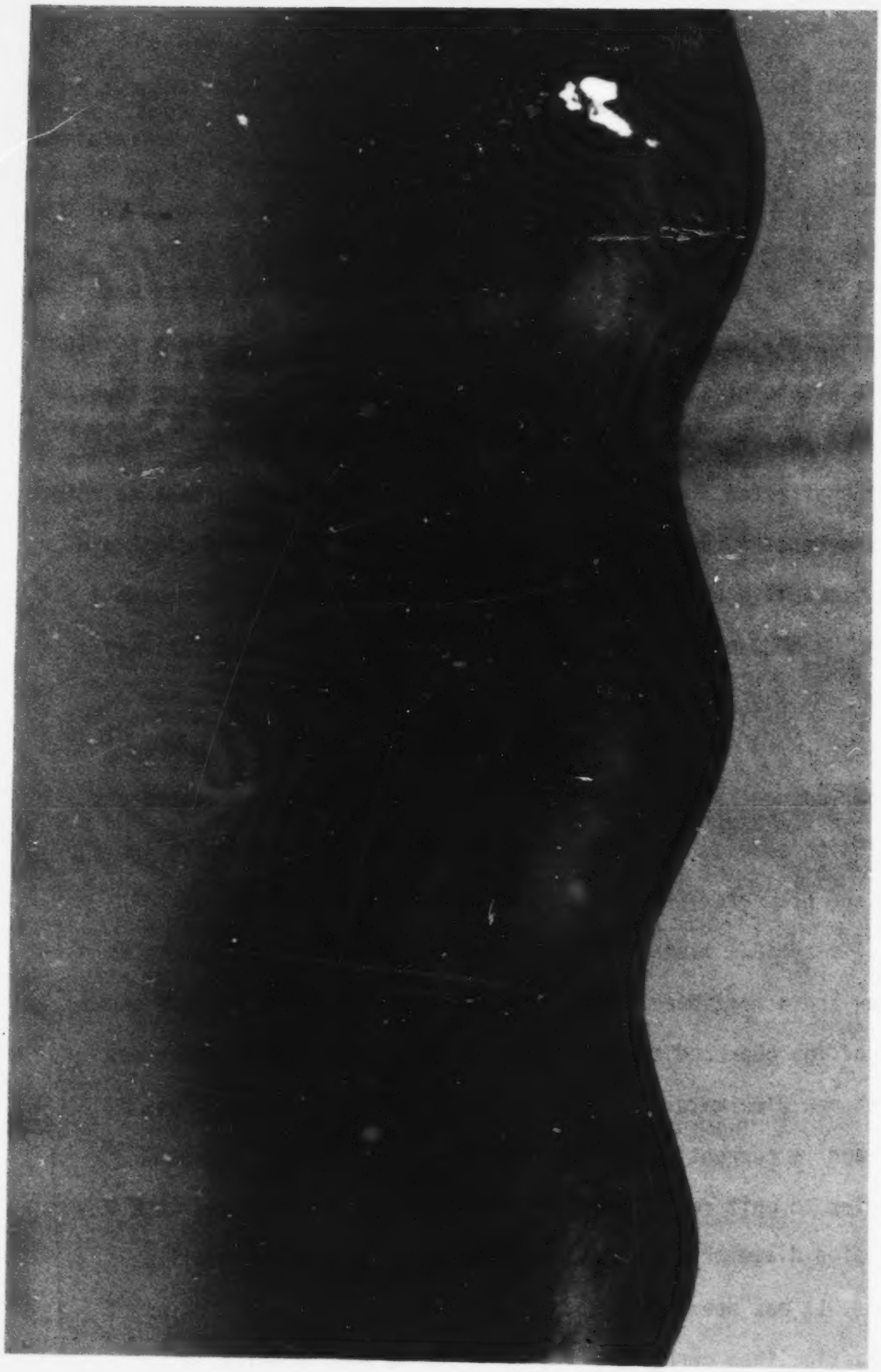

Figure 8. Corroded/eroded P-1 rotor

on the run conditions and the degree of previous chrome plating required on the specific rotor. Recently, the new Hastelloy-C rotor for P-1 was received and installed.

The last of the major problems encountered during RTU operation was that of reactor section corrosion. The 316L stainless steel primary reactor (R-1) and its attendant slurry circulating loops experienced pitting type corrosion. The severity of the pitting corrosion was found to be directly related to the affected area operating temperature. It is important to note that while the reactor section, which operated between 230°F and 270°F did corrode significantly, there was virtually no sign of pitting corrosion elsewhere in the RTU where slurry temperatures were generally maintained below 215°F.

The observed reactor section corrosion resulted in several instances of leach solution seepage from circulating loop piping during operation at temperature and pressure and resulted in unscheduled unit shutdown. A photograph of a typical seepage point is presented as Figure 9. Both an external view and a sectioned internal view of the seepage point are shown. As a result of the observed corrosion, all reactor associated piping was replaced with new 316L materials midway through the operational phase of the project and is currently scheduled for replacement with titanium materials prior to unit reactivation. Titanium is being utilized at RTU scale since pipe diameter dictates piping materials of solid metallic construction. It has been determined, however, that at larger scales of operation plastic lined carbon steel pipe would be most applicable.

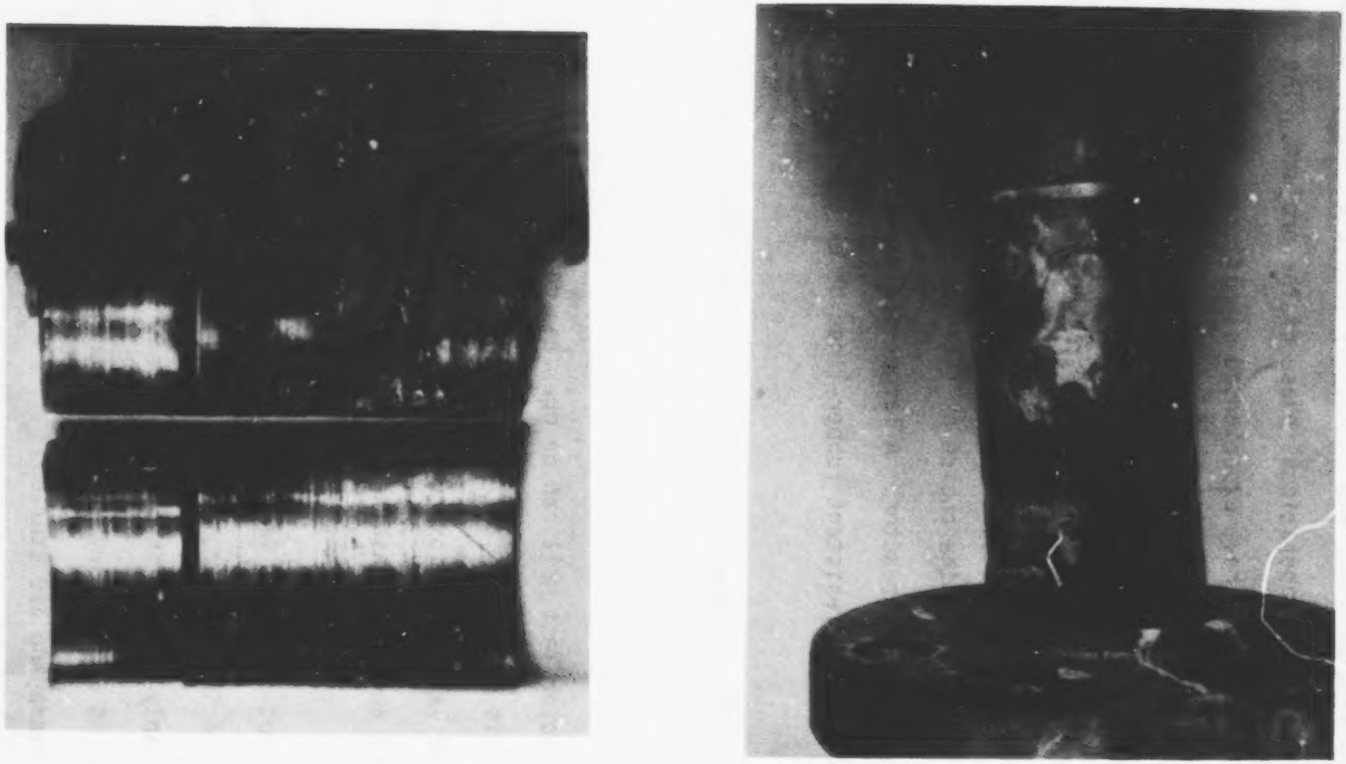

Figure 9. Flush port fitting

Primary reactor (R-1) was thoroughly inspected midway through and at the conclusion of the operational phase of the project. The internals of the unit were found to have experienced significant pitting corrosion. A photograph of the internals of the third stage of R-1, taken during the final inspection, is presented as Figure 10. Due to the extent of the observed corrosion, it is currently planned to install a replacement reactor of titanium construction prior to reinitiation of RTU operations. It is important to note that the choice of titanium is based on the relatively small size of the RTU reactor. A larger scale unit would no doubt be constructed of acid resistant rubber-lined brick over a carbon steel shell.

Overall RTU project conclusions are summarized below.

Operation Results

1. The Reactor Test Unit can be operated continuously for testing of the Meyers Process units for coal/leach solution mixing, simultaneous coal leaching and leach solution regeneration, filtration of leach solution from treated coal and water washing of coal on the filter.

2. The input coal from American Electric Power Service Corporation's Martinka mine in Fairmont, West Virginia, containing 1% inorganic sulfur can be reliably and continuously reduced, in the RTU, to a pyritic sulfur level of 0.16% without any measurable coal loss and with coal heat content increases averaging 350 Btu/lb.

3. RTU coal product, after bench-scale extraction of residual sulfate and elemental sulfur, was continuously and reliably reduced to a total sulfur

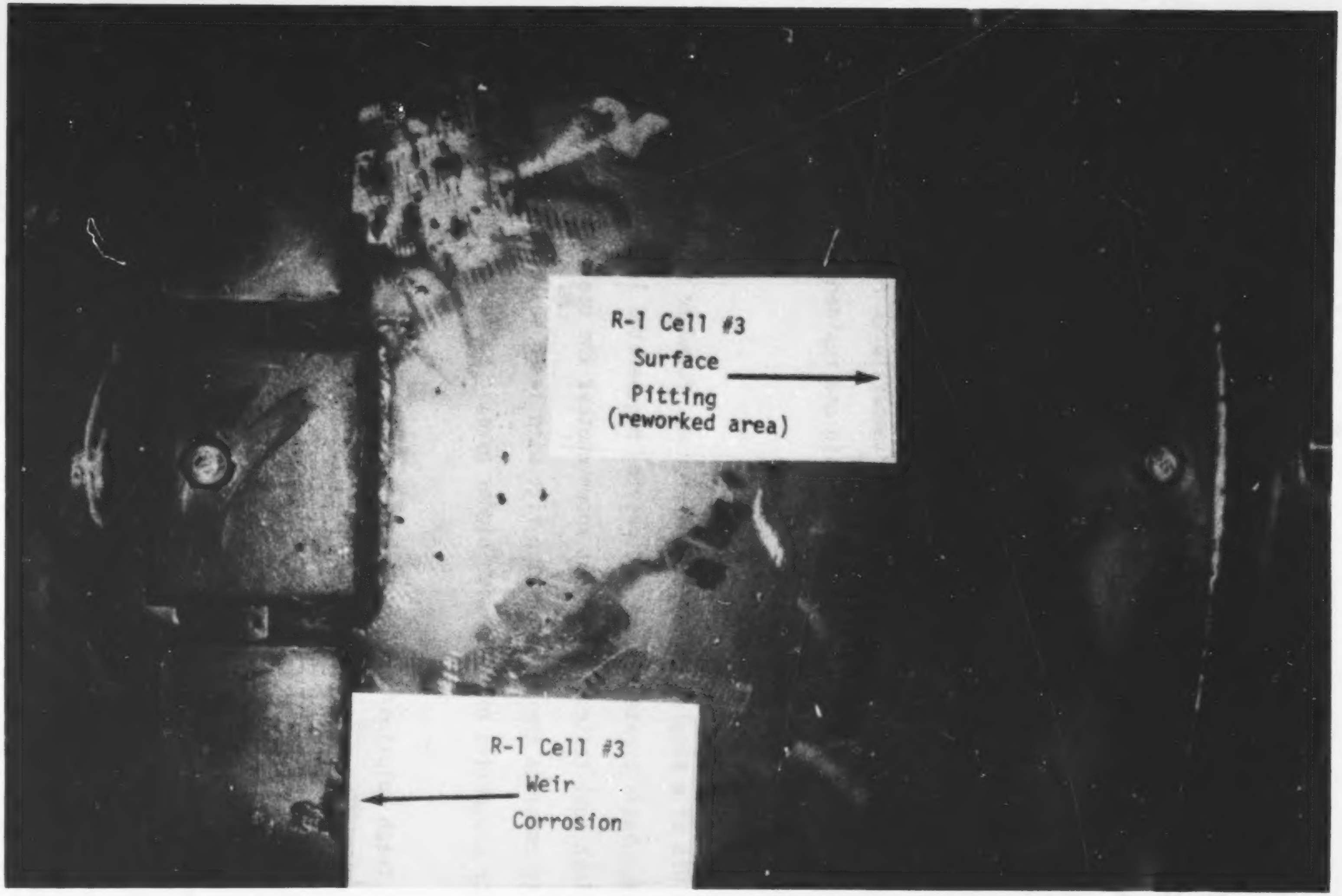

Figure 10. Primary reactor internal corrosion

content of 0.68-0.75% w/w and projected SO_x emissions levels of 1.0-1.2 lb $SO_2/10^6$ Btu.

4. Leach rates in the RTU were improved over bench-scale values by an average factor of 5, due mainly to favorable coal segregation in the primary reactor.

5. Plant leacher/regenerator operation at temperatures ranging 230° to 270°F (110° to 132°C), pressures of 30-80 psig and residence times of 5-8 hours was successfully demonstrated.

6. The use of a single reactor/regenerator was found to be sufficient to meet design basis pyrite removal and provide regenerated leach solution for the Martinka coal tested. It is not known whether the use of a secondary reactor to complete the reaction of pyrite with leach solution will be needed for processing of coals with higher pyritic sulfur content.

7. The leach solution/coal/oxygen environment caused corrosion in the primary reactor/regenerator system indicating that upgrading of the 316L material of construction is needed to support further testing.

8. The following materials were found to be suitable for leach solution/coal service at temperatures up to 90°C: fiber reinforced plastics, elastomers and 316L stainless steel. The following materials were determined to be suitable for service at reactor/regenerator temperatures up to 130°C: titanium, Hastalloy, and rubber-lined brick over mild steel.

9. No significant corrosion was observed in the leach solution/coal mix tank, flash-down tank, or storage tanks. Mild corrosion was observed in the reactor/regenerator pumps.

Supporting Experimentation Results

1. The iron sulfate/sulfuric acid leach solution can be used as a homogenous liquid to efficiently gravity-separate fine coal at specific gravities of 1.2 to 1.35.

2. Beneficial engineering cost improvements are obtained by using this gravity-separation technology to bypass a significant portion of the input coal around the reactor, elemental sulfur extraction and dryer units of the Meyers Process. This revised process is termed the Gravichem Process.

3. The Gravichem Process provides two products with no coal reject, a float coal containing 2-4% ash with almost no pyritic sulfur and a sink coal generally lower in ash than the input coal and also nearly pyrite-free. The two products can be used separately or combined.

4. Bench-scale testing of the Gravichem Process on the American Electric Power Service Corporation (Appalachian) coal gave two products: a float coal containing 1.0 lb $SO_2/10^6$ Btu and a sink coal containing 1.1 lb $SO_2/10^6$ Btu after treatment by the Meyers Process. Both products met present New Source Performance Standards.

5. Bench-scale testing of the Gravichem Process on a Tennessee Valley Authority (Eastern Interior Basin) coal containing 12% ash and 7 lb

$SO_2/10^6$ Btu gave two products: a 4% ash float coal containing 3 lb $SO_2/10^6$ Btu and a sink coal containing 4 lb $SO_2/10^6$ Btu and 11-12% ash after treatment by the Meyers Process.

6. The solvent system, acetone and water, is the most economically attractive method thus far investigated for removal of generated elemental sulfur from treated coal. This solvent also dissolves and removes residual iron sulfate.

Engineering Design Results

1. Process cost forecasts for the Gravichem Process are $68-69/KW capital cost with $0.44-0.50/10^6 Btu processing costs (including utility financed capital amortization for input coal costing $0.78-0.81/10^6 Btu).

2. Coal energy efficiency is 94-97% for the Gravichem Process including coal used for process heating.

3. Overall energy efficiency including both coal use and electric energy for plant operation is 93-96%.

PROJECT STATUS

In early 1978, the RTU coal desulfurization unit was secured for an extended shutdown period at the direction of the EPA. The extent of the shutdown period is currently unknown. Other aspects of the coal desulfurization project at TRW are continuing, however. Currently, work is focused on the further development of the Gravichem Process. The current efforts involve the accomplishment of additional bench-scale experimentation, full scale process engineering analyses, user specific applications studies, RTU equipment redesign and specification, RTU tail-end unit design, and RTU equipment preservation and maintenance.

In anticipation of restart of the RTU at a future date, the unit is being preserved and maintained in a standby condition to prevent corrosion and to limit system deterioration. The plant has been cleaned of residual leach solution and coal by flushing with water. Where appropriate, preservatives were added to protect against corrosion. All electrical equipment was shutoff and tagged; instrumentation was sealed and dessicant added. Liquid and solid wastes were hauled away. A detailed plant inspection will be performed to assess the degree of corrosion that has occurred. Preventive maintenance of the RTU is being carried out on a weekly basis. Engineering studies are to be performed which will, 1) establish specifications for a new reactor vessel R-1 and obtain cost estimates and time of delivery and installation, 2) result in a preliminary conceptual design for an RTU tail-end unit elemental sulfur extraction system, and 3) evaluate application of the Gravichem Process, based on data obtained from bench-scale tests, for use as a stand-alone plant or as integrated into a physical coal cleaning complex. A respecification of the R-1 reactor vessel will be developed for a replacement vessel to be constructed of material which will give long-term service. Designs for a tail-end elemental sulfur extraction system will include the use of acetone or methyl ethyl ketone and other solutions for removal of elemental sulfur at the RTU scale. Based on an early tail-end unit conceptual design effort, the RTU tail-end unit expansion is envisioned to appear as presented in Figure 11.

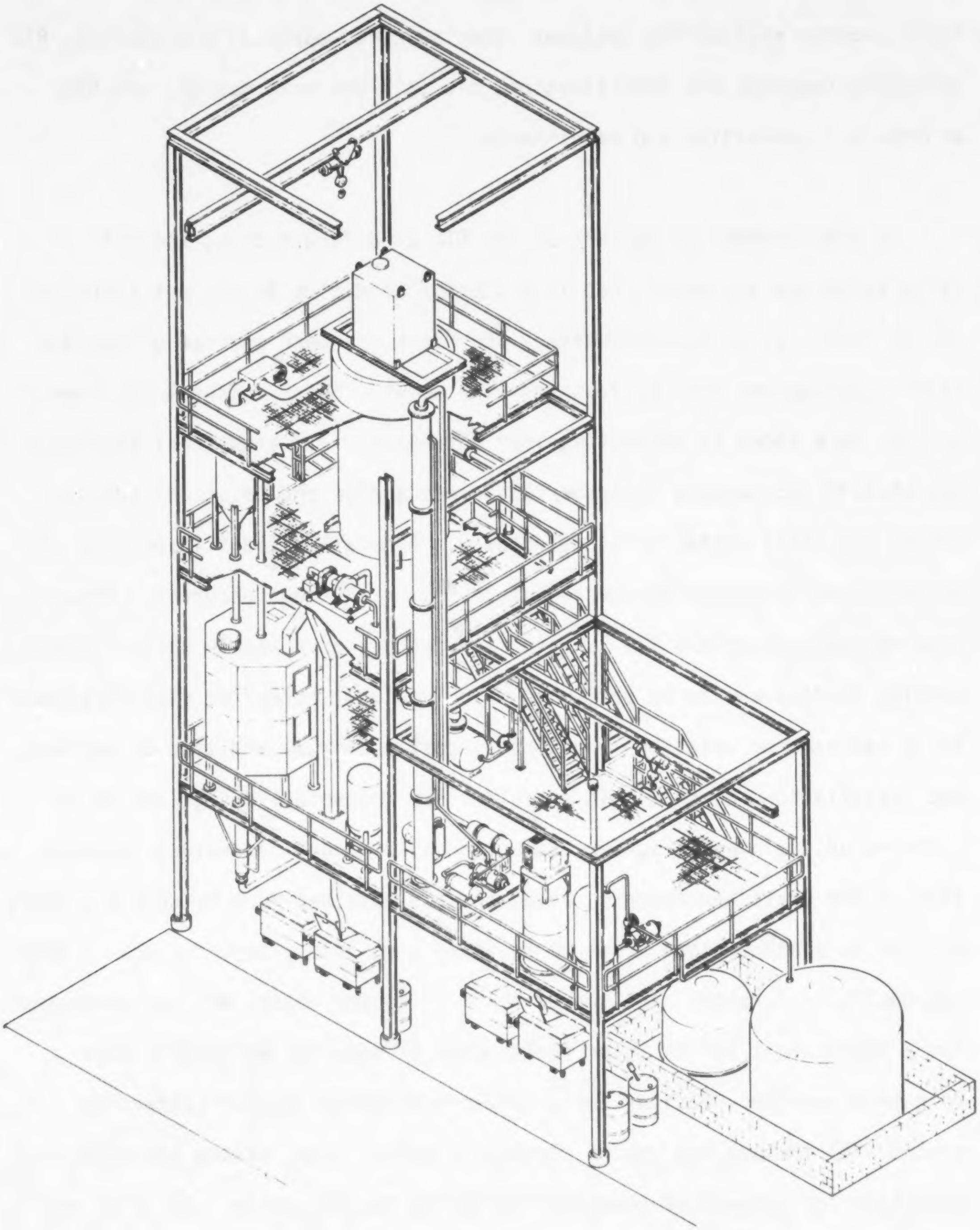

Figure 11. RTU tail-end unit expansion

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Metric Conversion Factors

In compliance with EPA policy, metric units have been used extensively in this paper. However, in some cases, British units have been used for ease of comprehension. For these cases, the following conversion table is provided:

British	Metric
1 Btu	252 calories
1 Btu	2.93×10^{-4} kilowatt-hours
1 KW	1,000 joules/sec
1 hp (electric)	746 joules/sec
1 psi	0.07 kilograms/cm^2
5/9 (°F-32)	°C
1 inch	2.54 centimeters
1 ft	0.3048 meter
1 ft^2	0.0929 meters^2
1 ft^3	0.0283 meters^3 or 28.3 liters
1 gallon	3.79 liters
1 pound	0.4536 kilograms
1 ton (short)	0.9072 metric tons

STATUS OF HYDROTHERMAL PROCESSING FOR CHEMICAL DESULFURIZATION OF COAL

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ABSTRACT

Chemical desulfurization of coal is achieved by heating an aqueous slurry of coal, sodium hydroxide, and calcium hydroxide in a closed vessel at elevated temperatures and corresponding steam pressure. Later, the cleaned coal product is separated from the spent leachant by a series of liquid/solid separations and utilized as a source of fuel. The spent leachant is regenerated for recycle.

This paper presents the current status of this technology and the results of a current study to improve the economic viability of hydrothermal cleaning by reducing the costs associated with liquid/solid separation and leachant regeneration.

INTRODUCTION

Results from a previous study for the U.S. Environmental Protection Agency - "Combustion of Hydrothermally Treated (HTT) Coals", Contract No. 68-02-2119 - indicated that HTT coals prepared by the Hydrothermal Coal Process from selected coals are clean solid fuels that in many instances can be burned with little or no sulfur emissions. Also, the HTT coals burn as well or better than raw coal and trace metal emissions should be significantly reduced because of the low concentrations in HTT coals.

This work is being continued under the program entitled "Process Improvement Studies on Battelle Hydrothermal Coal Process" (EPA Contract No. 68-02-2187). Under this program, emphasis has been on development of process improvements in the liquid/solid separation and leachant regeneration segments of the process. In the liquid/solid separation, laboratory and miniplant tests were performed to evaluate improvements which can be achieved by the use of larger coal particle sizes in combination with vacuum and centrifugal filtration and oil agglomeration. In leachant regeneration, a number of potential methods have been screened. Primary emphasis has been on the use of metallic compounds containing zinc and iron.

Technical progress during this contract are discussed in this paper.

Process Description

The Battelle Hydrothermal Coal Process (BHCP) is a method for producing environmentally acceptable solid fuels (clean coal) from high sulfur coals.

Basically, hydrothermal coal processing involves heating an aqueous slurry of coal and a chemical leachant, in this case, a mixture of sodium hydroxide and lime at moderate temperatures and corresponding steam pressures to extract the sulfur and some of the ash from the coal and subsequent regeneration of the leachant for recycle. The process entails five major processing steps as shown in Figure 1:

- Coal preparation
- Hydrothermal treatment (desulfurization)
- Fuel separation (separation of spent leachant from clean coal)
- Fuel drying
- Leachant regeneration.

Coal preparation entails crushing or grinding of the raw coal, as-received from the mine or after washing.

The coal is then mixed with the leachant, or, alternatively, the coal may be physically beneficiated to remove some of the ash and pyritic sulfur before mixing with the aqueous leachant.

After mixing with the leachant, the coal slurry is pumped continuously through the hydrothermal treatment (desulfurization) segment where it is heated to a temperature and corresponding steam pressure necessary to extract the sulfur.

The resulting coal-product slurry is then cooled and the cleaned coal is separated from the spent leachant by a series of washing - filtration operations.

Next, the desulfurized product is dried to reduce the residual moisture to the desired level.

In the basic process, the spent leachant is regenerated for recycle by the CO_2-CaO process. This entails sparging the spent leachant with carbon dioxide to liberate the sulfur as hydrogen sulfide, which is subsequently converted to elemental sulfur by the Claus or Stretford process. The carbonated liquor is then causticized with lime and filtered to remove the calcium carbonate which is calcined to produce lime and carbon dioxide for recycle. The regenerated leachant is concentrated and recycled to the process.

Process Chemistry

Sulfur Extraction

Sulfur is contained in coal in primarily two forms -- inorganic sulfur as FeS_2 (pyrites) which is associated with the mineral matter and

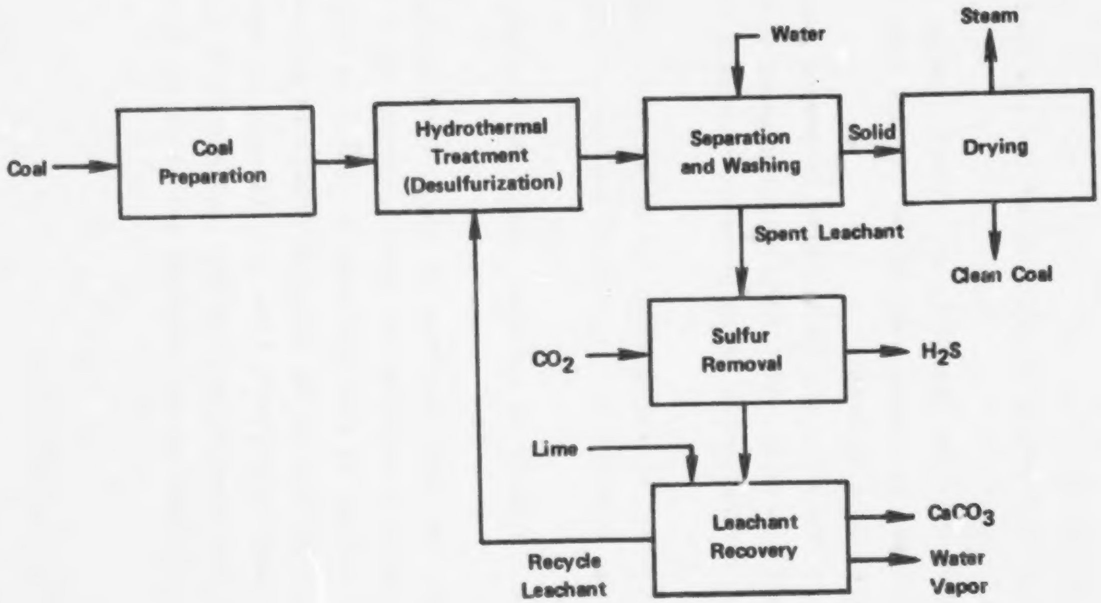

FIGURE 1. FLOW DIAGRAM OF THE BASIC HYDROTHERMAL COAL PROCESS

organic sulfur which is part of the coal molecule. During treatment of the coal by hydrothermal leaching, up to about 95 percent of the inorganic sulfur is extracted from most coals and up to 50 percent of the organic sulfur is extracted from some coals.

The dissolution or extraction of the inorganic sulfur from coal using alkaline leaching may involve several chemical reactions including the following:

(1) $FeS_2 + OH^- \rightarrow Fe(OH)_2 + S_2^{-2}$

(2) $2FeS_2 + 6OH^- \rightleftarrows Fe_2O_3 + S_2^{-2} + 2S^{-2} + 3H_2O$

(3) $3FeS_2 + 8OH^- \rightleftarrows Fe_3O_4 + S_2^{-2} + 2S^{-2} + 4H_2O$.

However, experimental studies on leaching of coal at Battelle have demonstrated that sulfur species found in the spent leachant is sodium sulfide, Na_2S, if the leaching is carried out to eliminate oxygen from the system. This data would indicate that the sulfur extraction mechanism may be as follows:

(4) $FeS_2 + 2NaOH \rightarrow Fe(OH)_2 + Na_2S_2$

(5) $Na_2S_2 + Fe(OH)_2 \rightarrow Fe_2O_3 + Na_2S$

or (6) $Na_2S_2 + \text{coal} \rightarrow CO_2 + Na_2S$.

In Reaction (4), the pyritic sulfur is extracted as the disulfide. The disulfide is then chemically reduced to form the sodium sulfide (Na_2S) by the ferrous hydroxide [$Fe(OH)_2$] (Reaction 5) or by the carbon in the coal (Reaction 6).

Mechanism for extraction of organic sulfur from coal has yet to be resolved. This could occur by cleavage of carbon to carbon or carbon to sulfur bonds. A simple organic sulfur compound ($CH_3 - S - CH_3$) has been identified in the gases evolved during desulfurization of the coal.

Leachant Regeneration

As discussed above under desulfurization mechanism, the spent leachant contains sulfide sulfur as Na_2S which must be removed in order to recycle the leachant. One approach for achieving this is by the CO_2-CaO process. This involves

(1) Liberation of the sulfide sulfur as H_2S by carbonation according to the following reactions

$$NaOH + Na_2S + CO_2 \xrightarrow{H_2O} H_2S\uparrow + NaHCO_3$$

$$NaHCO_3 + \Delta \rightarrow Na_2CO_3 + CO_2.$$

(2) Regeneration of NaOH by treatment of solution from (1) above with lime.

$$Na_2CO_3 + CaO \rightarrow CaCO_3 + NaOH.$$

(3) Regeneration of $CaCO_3$ for recycle by thermal decomposition

$$CaCO_3 + \Delta \rightarrow CaO + CO_2\uparrow.$$

Other potential approaches will be discussed later.

Process Improvements

Leachant Regeneration

The sodium sulfide (Na_2S) must be removed prior to recycle of the leachant. If not, the build-up of Na_2S will result in successively lower sulfur extraction as the leachant is recycled.

Under this program, a number of potential regenerates for regeneration of the spent leachant have been screened:

(a) Zinc Oxide (ZnO)

(b) Sodium Zincate (Na_2ZnO_2)

(c) Metallic Zinc (Zn)

(4) Metallic Iron (Fe)
(5) Ferrous Oxide (FeO)
(6) Ferrous Hydroxide [$Fe(OH)_2$]
(7) Ferroso-ferric oxide (Fe_3O_4)
(8) Ferric Oxide (Fe_2O_3)
(9) Ferric hydroxide [$Fe(OH)_3$]
(10) Hydrogen reduced/Oxidized Iron Oxide
(11) Sodium ferrite (Na_2FeO_2)
(12) Ferrous Carbonate ($FeCO_3$)
(13) Activated Carbon .

Effectiveness of Regenerates. A number of regenerates were found to be effective in removing greater than about 85 percent of the total sulfide sulfur from the spent leachant.

Zinc-Containing Materials. The addition of zinc oxide, sodium zincate and metallic zinc to the spent leachant results in the formation of an insoluble zinc sulfide. As noted in Figure 2, zinc oxide at ZnO/S ratios of 1.25 to 1.75 resulted in the removal of greater than 85 percent of the sulfide sulfur in approximately 20 minutes at 80 C. At a ZnO/S ratio of 3, 100 percent of the sulfide sulfur was precipitated in less than 10 minutes. At 40 C, ZnO was still effective, but longer time was required to achieve a high degree of sulfide removal. Zinc metal was also effective. However, larger Zn/S ratios were required because of the lower surface area.

Iron-Containing Compounds. A number of iron-containing compounds have been investigated for regeneration of the spent leachant. Of these, iron hydroxides, reduced/oxidized iron oxide, and ferrous carbonate are the most effective as noted in Figure 3.

Ferrous carbonate ($FeCO_3$) is the leading candidate. As shown in Figure 4, 80 to 99 percent of the sulfide sulfur is precipitated in less than 15 minutes depending on the Fe/S ratio and source of $FeCO_3$.

The use of the carbonate makes use of known chemistry. The sulfide sulfur is precipitated from the spent leachant by the following reaction:

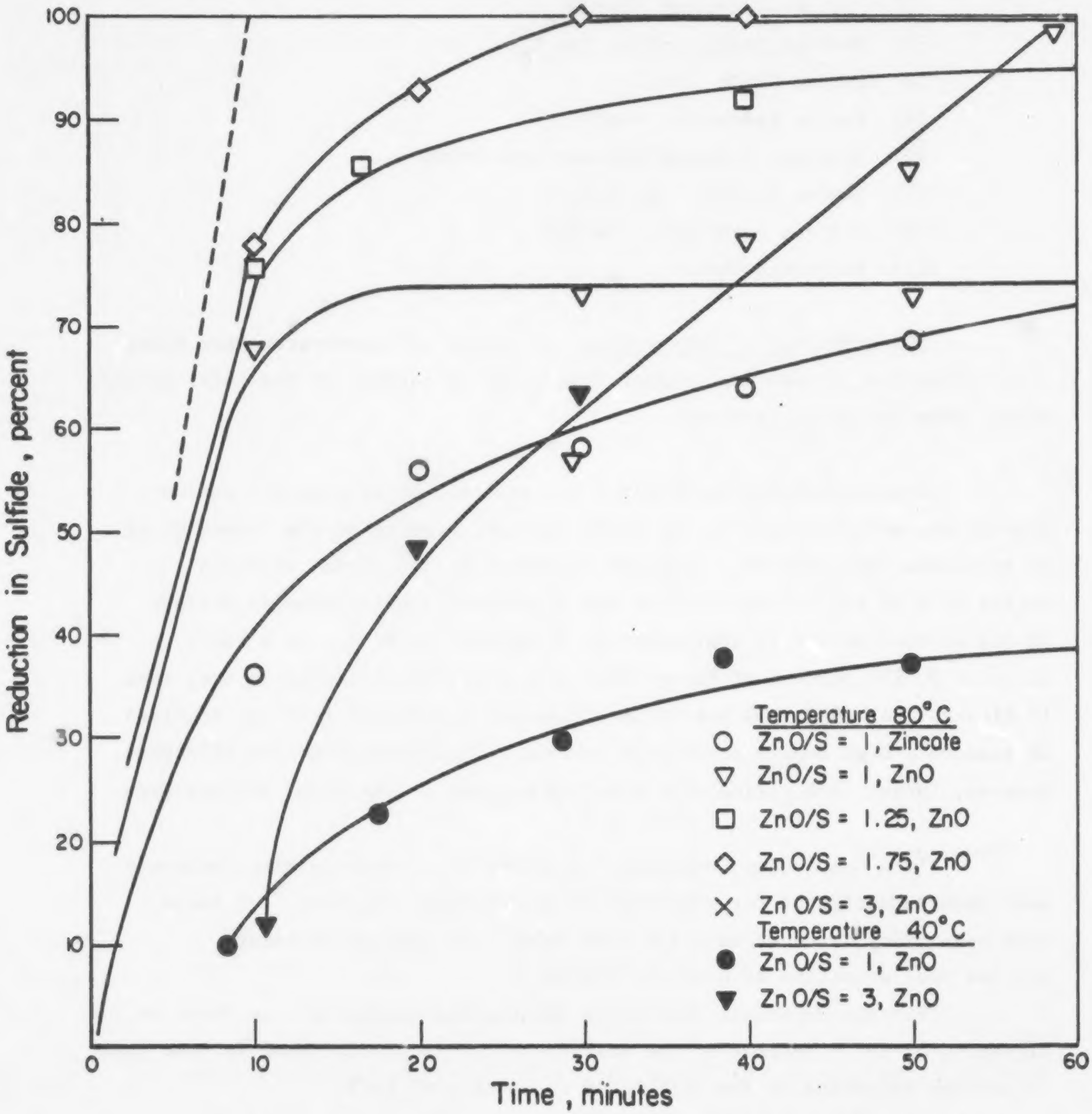

FIGURE 2. LEACHANT REGENERATION WITH ZnO (BATCH REACTION) AND ZINCATE

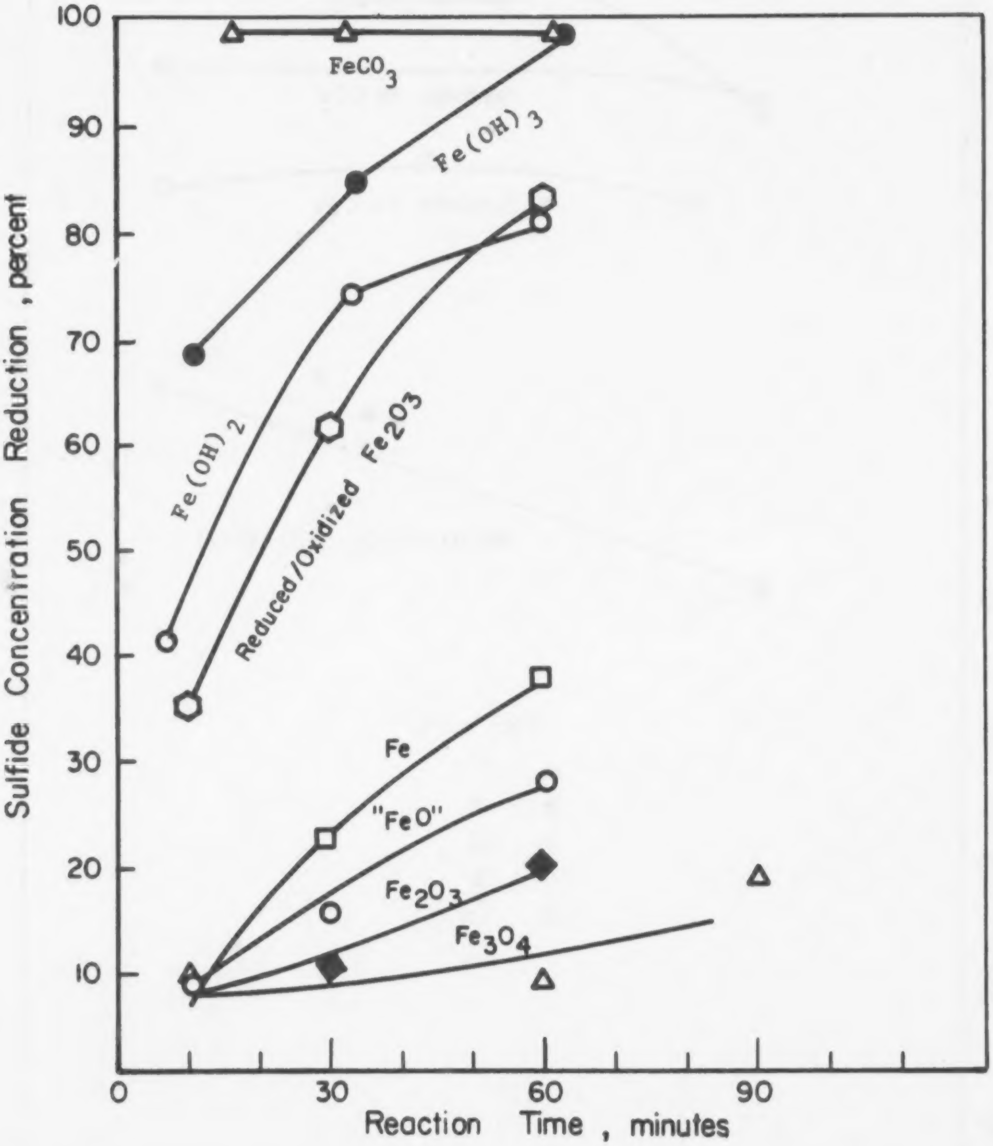

FIGURE 3. EFFECT OF VARIOUS FORMS OF IRON ON SULFIDE REDUCTION

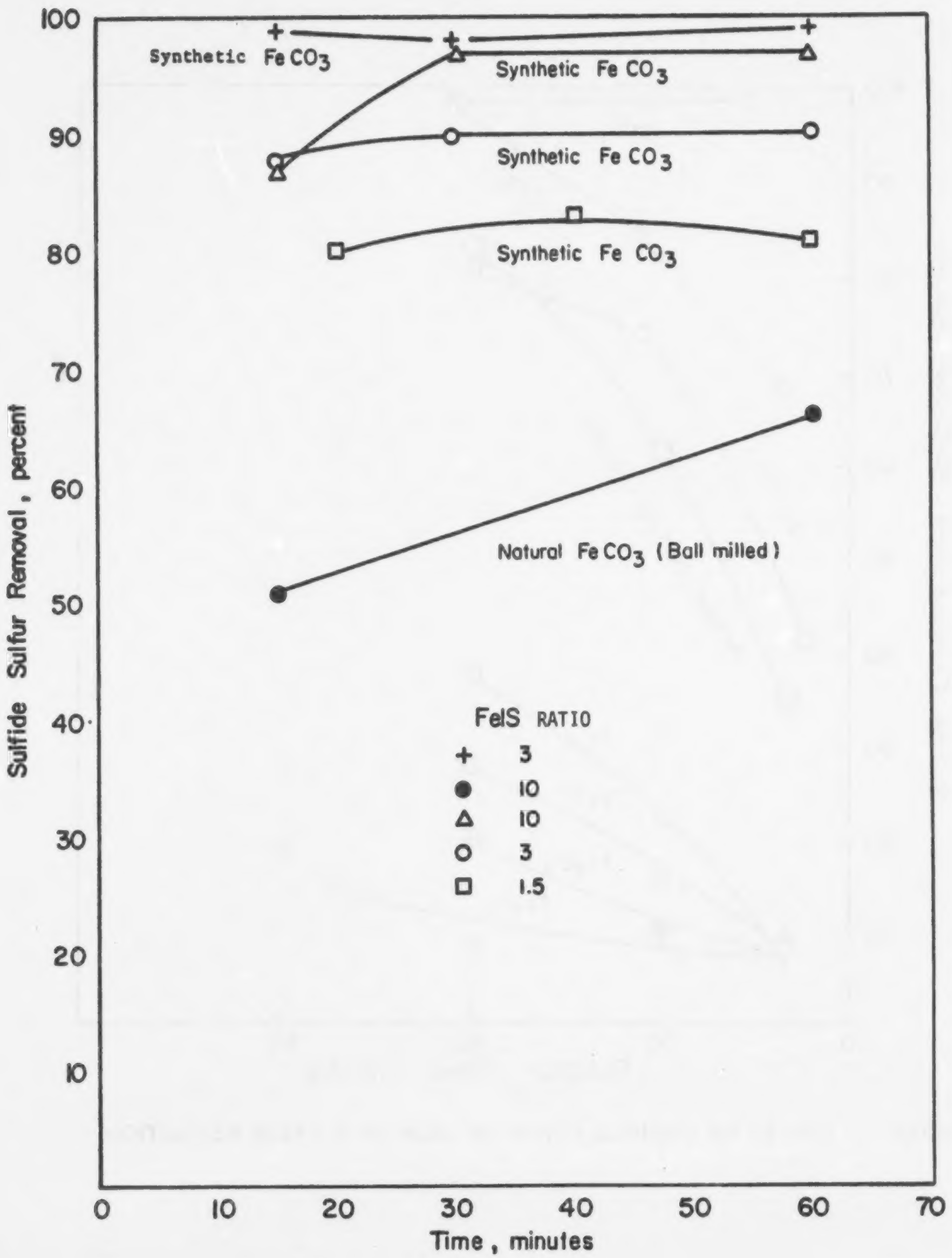

FIGURE 4. SULFIDE SULFUR REMOVAL WITH FERROUS CARBONATE

$$FeCO_3 + (Na_2S - NaOH) \rightarrow FeS\downarrow + (Na_2CO_3 - NaOH).$$

The regenerated leachant will contain some Na_2CO_3. This can be removed by the addition of lime (CaO) which results in the precipitation of an insoluble calcium carbonate.

The iron values may be regenerated for recycle accordingly:

$$FeS + 2O_2 \xrightarrow{H_2O} FeSO_4$$

$$\underline{FeSO_4 + Na_2CO_3 \rightarrow FeCO_3 \downarrow + Na_2SO_4}$$

$$FeS + 2O_2 + Na_2CO_3 \xrightarrow{H_2O} FeCO_3 \downarrow + Na_2SO_4$$

Reduced/oxidized ferric oxide, i.e., a ferric oxide which is first reduced with hydrogen to a pyrophoric state and then partially oxidized effectively removes the sulfide sulfur from the spent leachant. As shown in Figure 5, 80 to 90 percent of the sulfide sulfur was removed by contacting the spent leachant with the reduced oxide for a period of 60 minutes.

Preliminary results indicate that the spent reduced oxide can be regenerated for recycle. As shown in Figure 6, first regenerated iron oxide was as efficient as the original reduced/oxidized iron oxide. The material regenerated the second time showed a slightly lower activity after the reduction/oxidation treatment. However, this may be due to a lower Fe/S ratio--11 compared to 8.

Freshly prepared iron hydroxides also separate the sulfide sulfur from the spent leachant. At room temperature, 98 percent of the sulfur (Figure 7) was removed in 1 hour at an Fe/S ratio of 3 with ferric hydroxide When the reaction temperature was reduced to 0 C, 90 percent of the sulfur was removed. At 80 C, reversal of sulfide removal was suggested. Ferrous hydroxide appears to be less effective than ferric hydroxide as shown in Figure 3. The primary disadvantage of these materials is that the spent hydroxides are not readily regenerated for recycle.

Liquid/Solid Separation

The coal product slurry from the desulfurization segment of the BHCP contains (1) desulfurized coal and (2) spent leachant. This slurry is

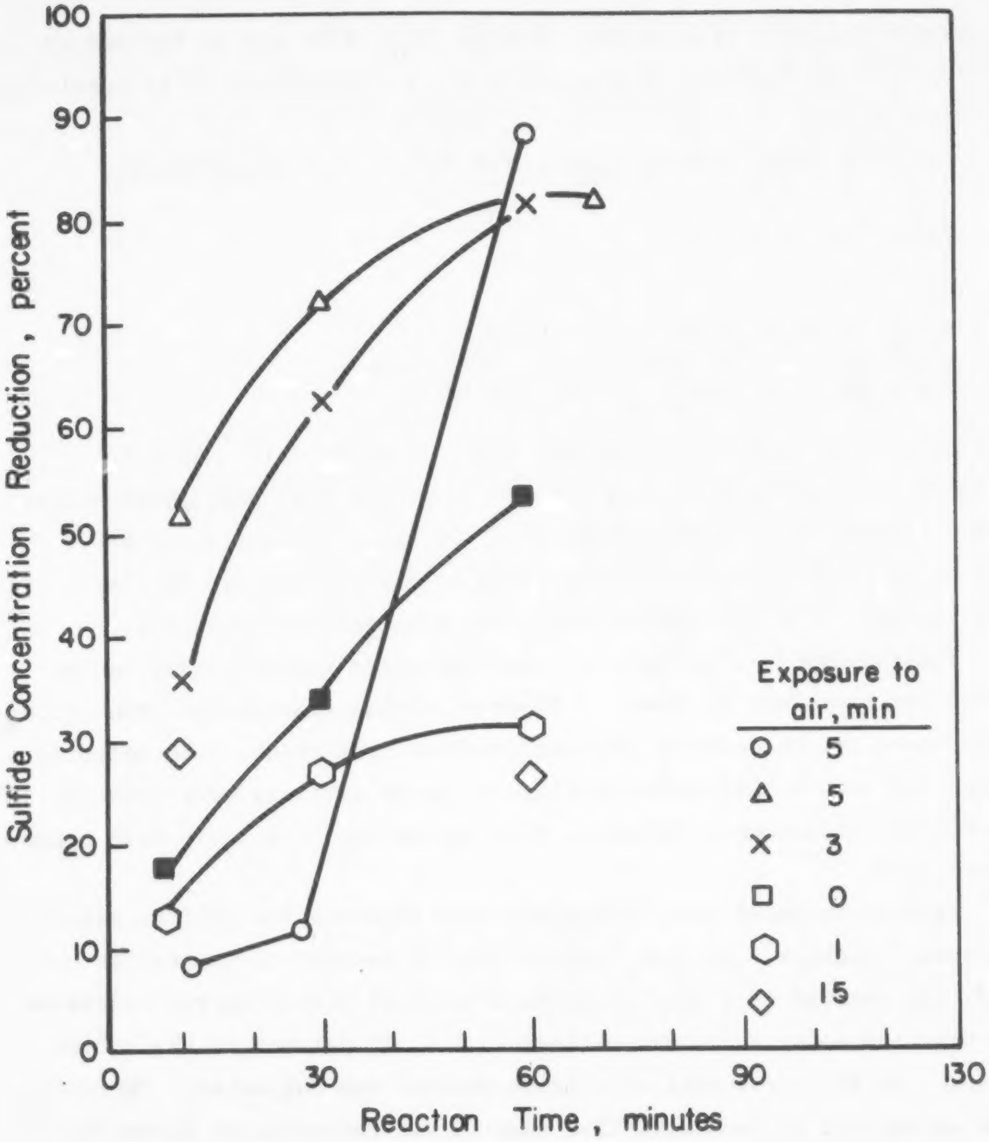

FIGURE 5. EFFECT OF THE PERIODS OF EXPOSURE TO AIR OF REDUCED IRON OXIDE ON REDUCTION IN SULFIDE CONCENTRATION

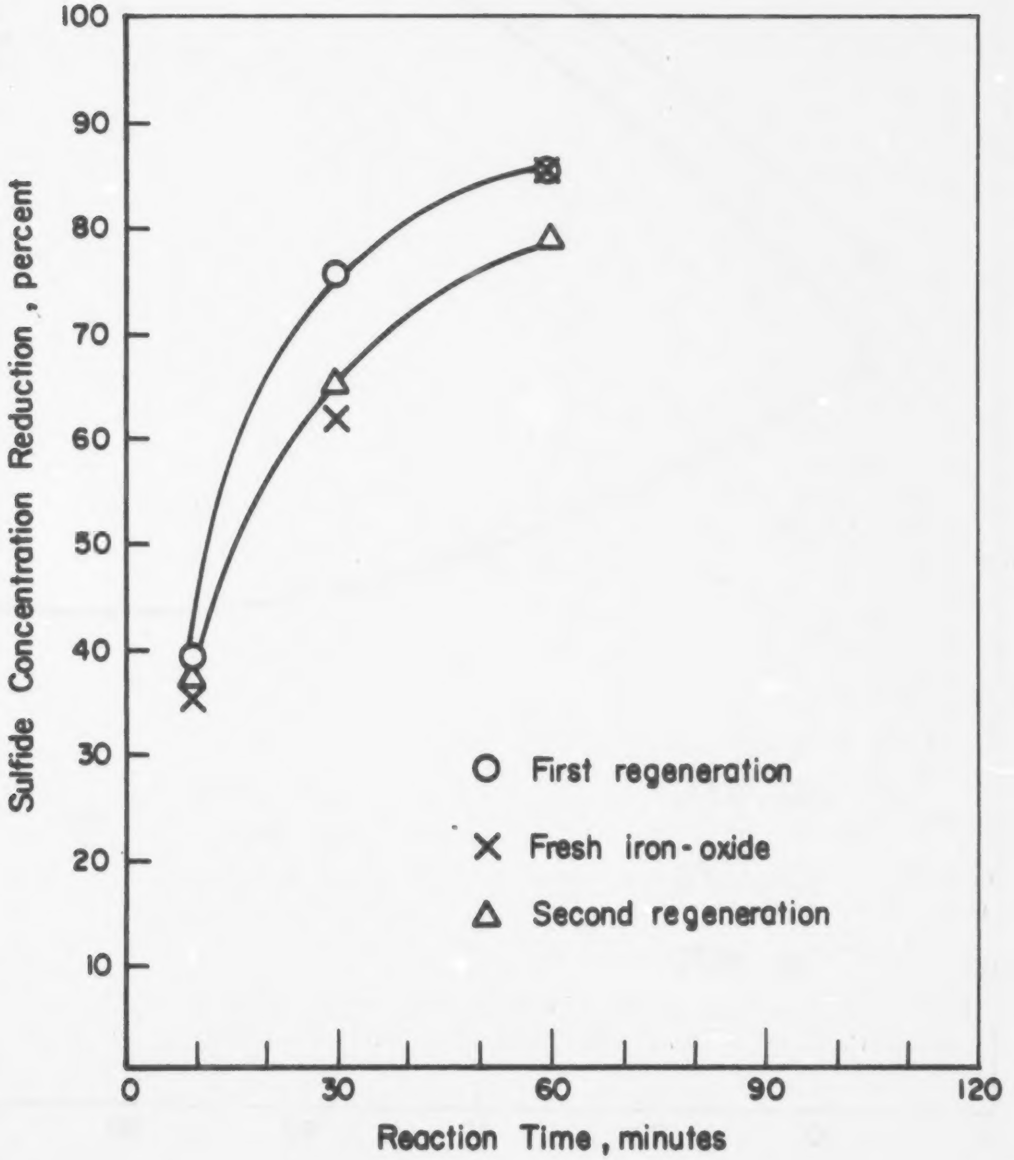

FIGURE 6. **EFFECT OF REGENERATION OF SPENT IRON OXIDE**

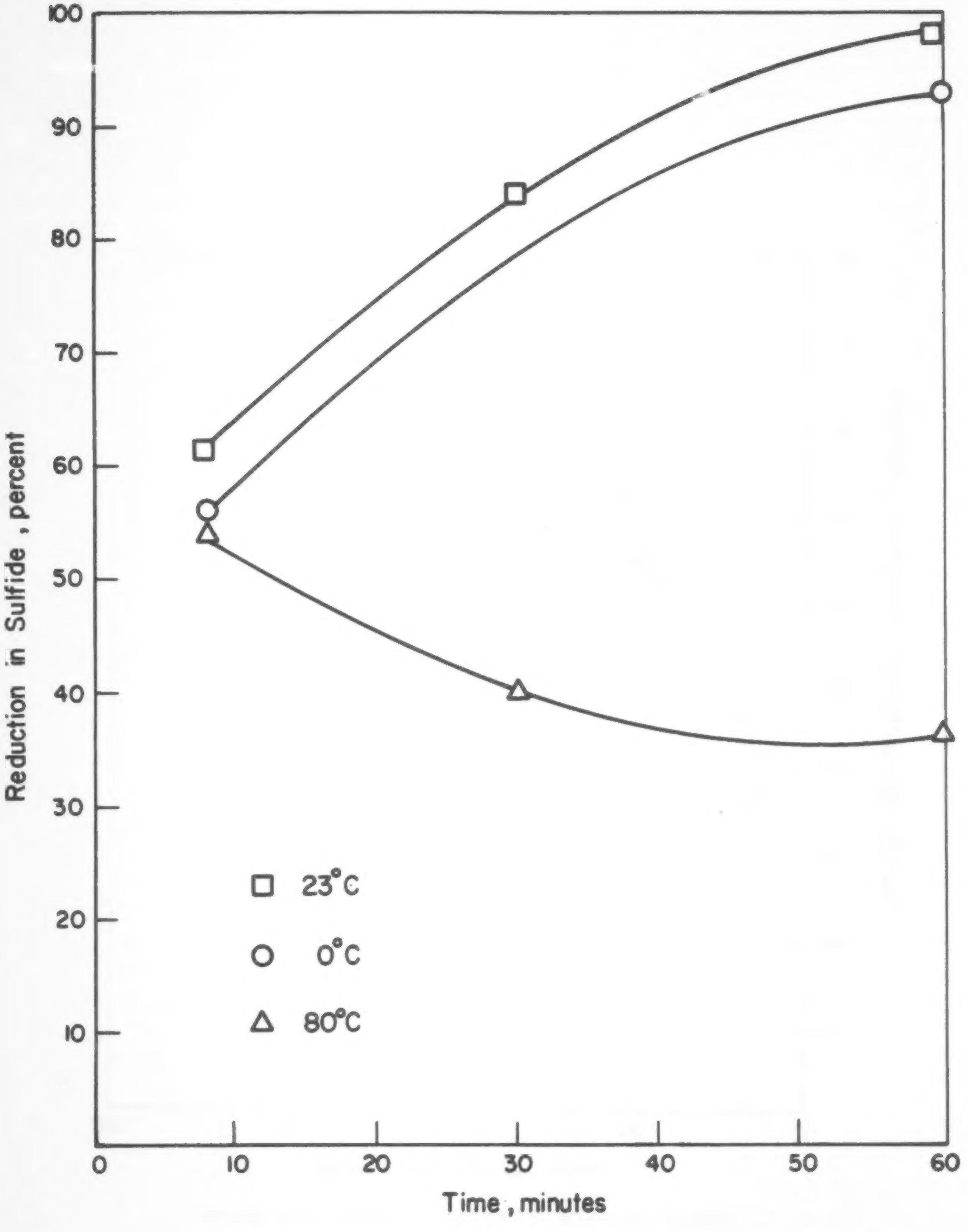

FIGURE 7. THE EFFECT OF TEMPERATURE ON LEACHANT REGENERATION WITH $Fe(OH)_3$

first filtered to remove the primary filtrate from the cleaned coal product. This material is then washed to separate the residual spent leachant from the clean (HTT) coal.

In the initial development of the BHCP, 70 percent minus 200 mesh coal was used. This resulted in a HTT coal containing equal to or greater than 50 percent moisture and large quantities of water were required to separate the residual spent leachant from the HTT coal. Also, the liquid/solid separations proceeded slowly.

Analysis of this segment of the process indicated that process improvements -- reduced water consumption and lower water content of the coal product -- might be realized by the use of larger particle size coal. Therefore, a study was conducted to

- Increase liquid/solid separation rate
- Reduce moisture content of HTT coal product
- Minimize wash water consumption and
- Maximize sodium removal and

thus determine a near-optimizing separation and washing circuit. Two sizes of coal were examined -- 100 percent minus 20 percent and 100 percent minus 50 mesh.

Approach. Because of the large scale nature of the planned application and the slow to moderate separation rate, separation by large, commercially available equipment was selected for intensive study. The use of filtration aids, surfactants, and oil agglomeration to improve separation rates and final cake moisture were also studied.

Because of the complex nature of the separation and washing circuit and its interactions with other cost sensitive sections of the BHCP, a computer program was prepared to investigate the relationships between the total separation and washing costs and the following processing variables:

(1) Separation equipment (vacuum and belt filter, plus centrifuge)
(2) Separation rates
(3) Cake solids content
(4) Wash water-to-coal ratio
(5) Number of washing stages

(6) Residual unbound sodium.

Sensitivity studies allowed rapid investigation of the different separation techniques and showed where the most significant cost saving could be obtained.

Technical Achievements. **Through the use of coarser coals (-20 and** -50 mesh coal as compared to -200 mesh) and other process modifications, significant process improvements were realized.

Separation Rate. When the original -20 mesh solution was tested, a rate of only 0.008 ton/hr/ft^2 was obtained. Pretreatment testing was first conducted to improve the rate. The use of flocculants resulted in floating of the fines, allowing the coarser material to settle. Consequently, the fines settled on the surface of the cake, resulting in an effective barrier to further dewatering. Dispersants (sodium lauryl sulfate was found most effective) were found to solve this problem by dispersing the fines throughout the cake. Separation rates were increased by a factor of 10 to 0.08 ton/hr/ft^2 at an addition level of 0.5 lb/ton.

After the initial dispersant addition, separation rate was found to be primarily dependent on the degree of washing, increasing after each wash until it leveled off at >0.6 ton/hr/ft^2. Results with -20 and -50 mesh HTT coal are summarized in Table 1. As noted in the table, the degree of washing also has a strong effect on the final moisture content of the coal product.

Moisture Removal. The original separation tests with -20 mesh coal produced a cake with $\simeq$ 59 percent moisture. The use of dispersants for separation rate improvement also improved the moisture removal efficiency during separation. The cake showed lower moisture retention with the smaller -50 mesh coal. However, this trend to less moisture retention with smaller particle sizes did not extend downward to the -200 mesh coal where $\simeq$ 60 percent moisture cakes were produced . Since the separation rates with the -50 mesh were not significantly less than with the -20 mesh coal, this size range seemed near optimal for further development work.

Other measures to further reduce the moisture content included oil agglomeration prior to separation, solvent displacement, and centrifugation. The oil agglomeration tests showed that increased separation rates

TABLE 1.

VACUUM FILTRATION RATE AS A FUNCTION OF PARTICLE SIZE AND WASHING STAGE[a]

	Ground -20 Mesh		Ground -50 Mesh	
Washing Stage	Rate, kkg/hr/m^2 (ton/hr/ft^2)	Moisture Level, percent	Rate, kkg/hr/m^2 (ton/hr/ft^2)	Moisture Level percent
Initial separation	0.78 (0.08)	53	0.78 (0.08)	48
First wash	0.88 (0.09)	53	1.95 (0.2)	49
Second wash	2.93 (0.3)	54	2.93 (0.3)	50
Third wash	5.86 (0.6)	54	5.86 (0.5)	51
Fourth wash	>5.9 (>0.6)	55	5.86 (0.6)	52

(a) Vacuum filtration employing 28 in. Hg vacuum. Slurry initially treated with a sodium lauryl sulfate dispersant to improve water removal.

of 1.9 tons/hr/ft^2 could be obtained; however, the moisture content of the clean coal was reduced by only 1 to 3 percent. A washing test with a mixture of toluene and ethyl alcohol was conducted on a high moisture extensively washed cake. The solvents effectively displaced the water from the cake but did not reduce the moisture content of the coal product. Drying tests with the solvent washed coal showed that drying energy requirements were reduced in half as compared to the water washed coal.

For centrifuge testing, HTT coal was prepared in the continuous 30 lb/hr miniplant. A 6-14 bird screen bowl centrifuge was continuously fed with the miniplant output. While the centrifuge equipment was considered too small to generate accurate separation rate data, the test program did establish that the final moisture content could be lowered to $\simeq$ 40 to 42 percent.

Sodium Removal. The residual sodium remaining in the treated coal must be reduced for economic reasons (for sodium recycle and reuse) as well as combustion (corrosion) considerations. The sodium can be removed by displacement or repulp washing. Displacement washing occurs by the wash liquor pushing the filtrate ahead of it through the void channels with practically no filtrate dilution. In experimental testing, it was established that the HTT coal cake, due to its compressive nature resulting in low sodium removal and low separation rates, and thus, was not amenable to this washing technique. Therefore, emphasis was placed on repulp washing.

Repulp washing consists of mixing the separated filter cake with wash liquor and refiltering. The process eliminates stratified regions in the cake that are washed at different levels, assures close contact of the wash liquor and the soluble materials, increases the rate of diffusional extraction and, with proper media selection, can allow selective removal of slow filtering fines. This method of washing can be incorporated into a washing circuit employing almost any type of separation equipment. It is especially suited for counter-current "extraction" washing. Counter-current extraction offers the most economical use of wash liquor, permitting high sodium concentrations in the final extract sent to the evaporator and regeneration, and high solute recovery from the treated coal with a minimal amount of fresh wash water. Stepwise counter-current extraction is commercially employed for leaching of solids and washing of precipitates.

The washing scheme developed for HTT coal consists of a number of separation stages in series. Fresh wash water is mixed with the treated coal which has been most nearly exhausted of residual sodium. The filtrate from that operation is advanced progressively from one separation stage to the next until the most concentrated solution discharges from the separation stage where the fresh HTT coal slurry enters. Simultaneously the separated solids are transferred from one stage to the next in the opposite direction finally exiting from the fresh water washing stage. Because of the difficulty of simulating a multistage counter-current washing circuit, washing tests were conducted by repulp washing of the separated solids with fresh wash water rather than washing with filtrate from consecutive washing.

The first variable studied was coal particle size. It was theorized that the smaller particles could be washed easier because more of the sodium would be on the surface with less inside the coal particle. As noted in Figure 8, the smaller -100 mesh particles were more readily washed than the larger particles. The difference while significant was not sufficiently large to stop work on alternate methods of washing the larger, more rapidly filtering coal particles. A series of tests with the -50 mesh coal were conducted using a 2 to 1 water-to-coal ratio employing (1) extended (1 hr) mixing time to allow a longer time for diffusional controlled removal of the sodium, (2) a saturated CO_2 water wash to react with the sodium, and (3) a saturate lime water wash to promote greater ion exchange between the calcium and sodium.

The results are displayed in Figure 9. Clearly the saturated lime water wash was superior to the standard washing results. Apparently the dissolved calcium in the lime water promoted effective exchange with the sodium. In fact, the bound sodium (sodium not removable by extensive wash) was lowered from $\simeq$ 0.5 to $\simeq$ 0.1 percent. This result was especially signifi-

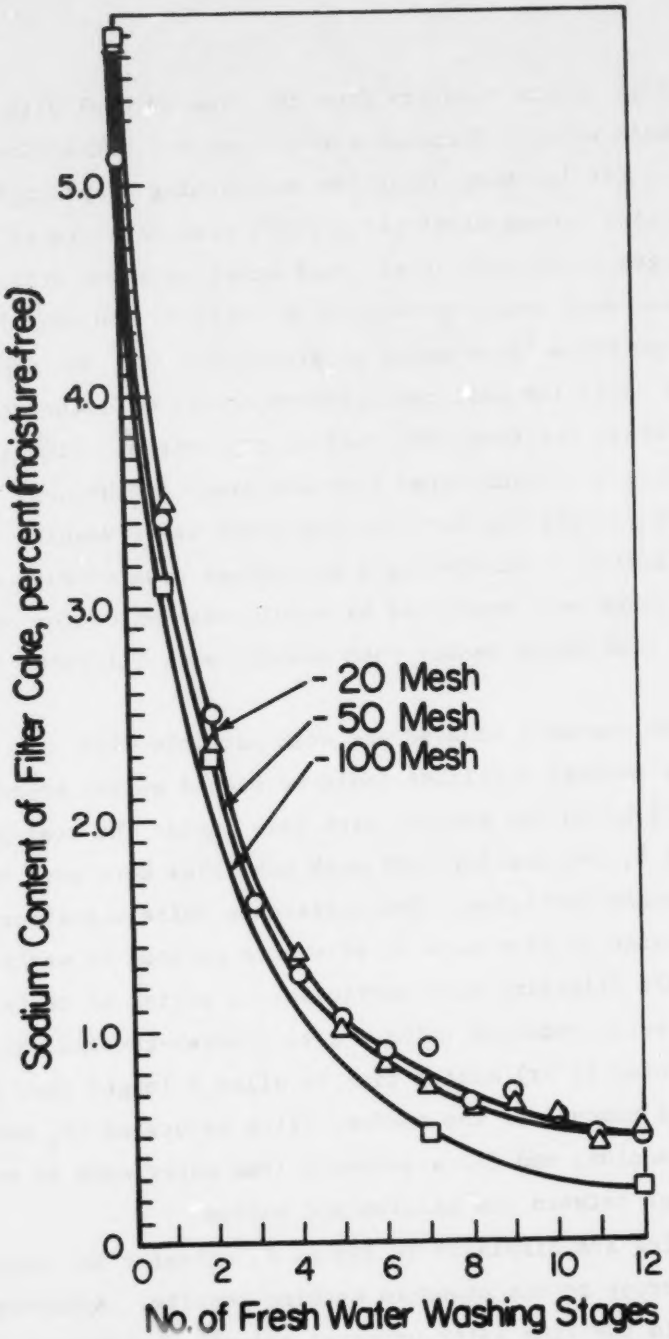

FIGURE 8. SODIUM REMOVAL VERSUS NUMBER OF WASHING STAGES AS A FUNCTION OF STARTING COAL PARTICLE SIZE

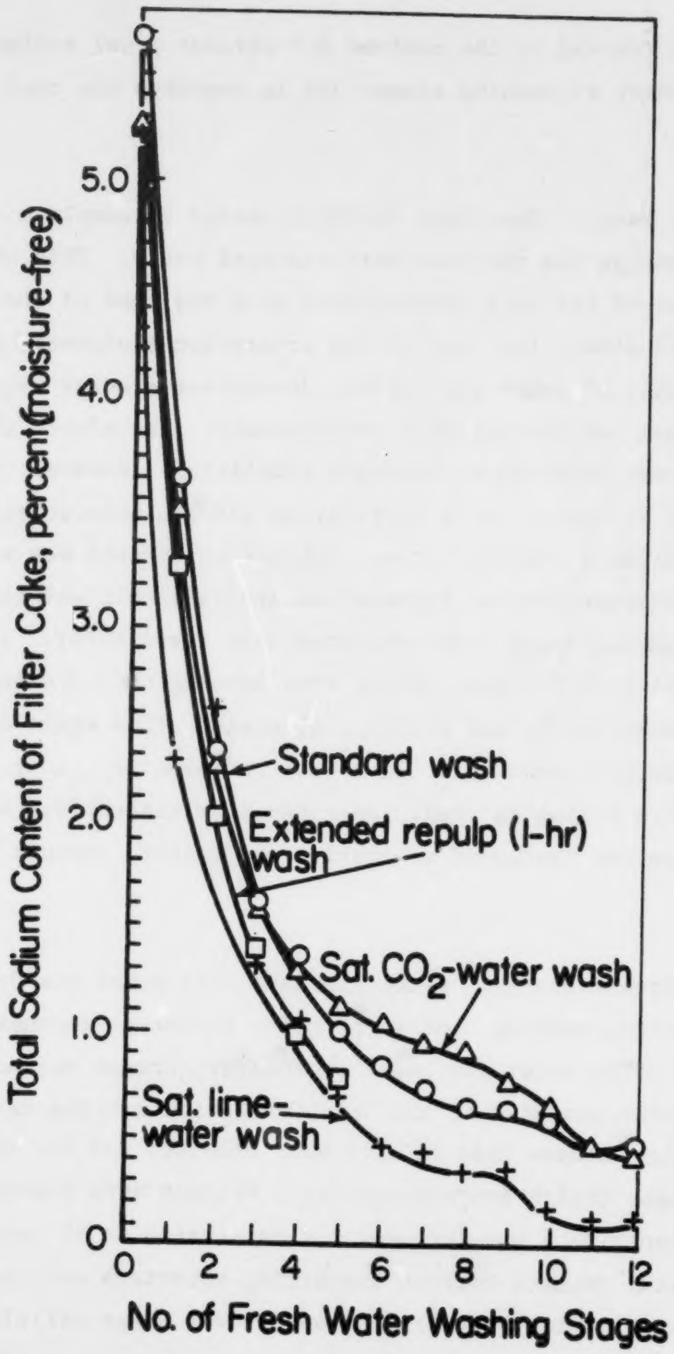

FIGURE 9. SODIUM REMOVAL VERSUS NUMBER OF WASHING STAGES FOR -50 MESH HTT COAL AS A FUNCTION OF SPECIAL WASHING METHODS

cant since it allows removal to the desired 0.5 percent total sodium level with a reasonable number of washing stages and impregnates the coal with a sulfur getter.

Wash Water Usage. The final variable needed to complete the L/S separation circuit design was the wash water-to-coal ratio. This is a complex variable because of its many interactions with the rest of the BHCP. The ratio chosen will effect the size of the separation equipment, number of stages, size and number of pumps and piping, downstream storage requirement as well as evaporation and regeneration requirements. Therefore, the wash water-to-coal ratio was selected by computer simulation. However, before the simulation could be conducted, a correlation between theoretical and actual sodium removal in a counter-current extraction circuit was required. Because multistage counter-current extractions are difficult and time consuming to conduct washing tests were conducted with fresh water. It was found that approximately 2.5 actual stages were necessary to obtain the same sodium removal as predicted by one theoretical stage. This stage efficiency was found to be a constant even up to 10 repulp washes (i.e., 10 repulp washes removed as much sodium as predicted after four theoretical washes). With this information the "optimum" separation and washing circuit was designed.

Washing Circuit Design. A computerized cost model was designed to simulate the separation, washing, and evaporation (prior to regeneration) section of the BHCP. The model was based on counter-current extraction washing of the solution produced in the desulfurization autoclaves. For the initial slow filtering stages disc filters were selected and for the more rapid filtering stages (fifth and higher), belt filters were chosen. A final stage screen bowl centrifuge was included for dewatering to 42 percent moisture. Theoretical counter-current extraction equations were adjusted to allow for the experimentally determined 40 percent stage efficiency.

The optimum circuit design depends on the bound sodium level. A relatively conservative level of 0.27 percent was specified. Based on the experimental data generated, the filter and centrifuge cake moisture content levels were set at 52 and 42 percent, respectively. The optimum design, displayed schematically in Figure 10 consists of a counter-current washing circuit composed of the following separation elements:

(1) Four disc filter stages

(2) Six belt filter stages

(3) One centrifuge stage.

A wash water-to-coal ratio of 1.75 was required to produce a final product with 0.47 percent (moisture free basis) total sodium.

Sodium, Ash, and Sulfur Levels. Chemical analyses of the raw and a typical product cake are summarized in Table 2. Three components are of special importance. First, the total sodium is below the desired 0.5 percent required for satisfactory boiler operation. Second, the ash content is slightly lower than that of the raw coal. Since both calcium and sodium levels are higher than in the starting coal, the reductions in ash are due to removal during the desulfurization step and subsequent downstream processing. Finally, and of great importance is the MAF sulfur level. Since the process goal is desulfurization, the product coals sulfur content must be below the NSPS level. At 0.86 percent MAF sulfur, the coal does meet this criterion. In addition, the high residual calcium level has been shown to lead to in-situ sulfur capture making the combustion off-gas even lower in SO_2 than that anticipated from the coal's sulfur content.

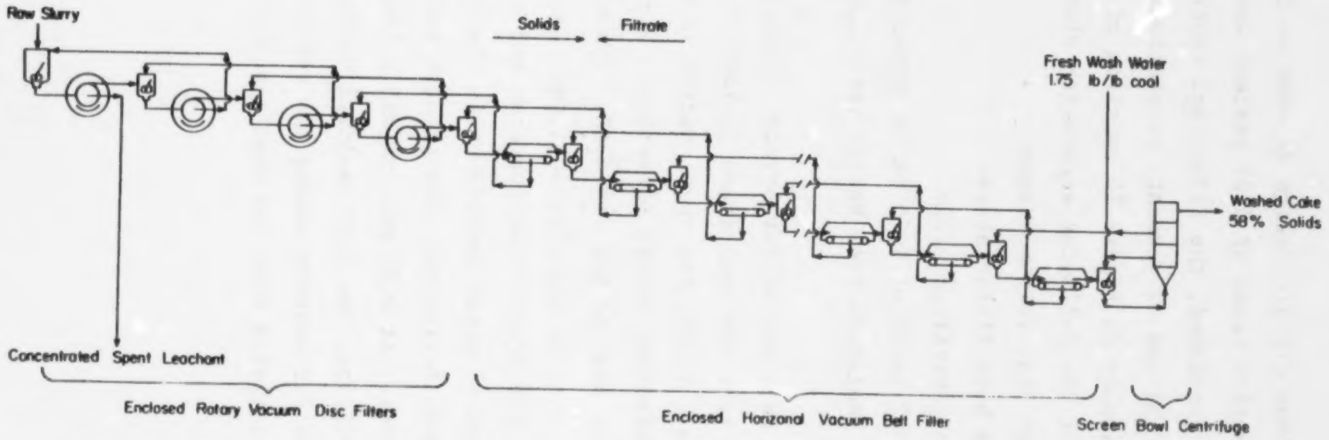
Raw Slurry
Solids
Filtrate
Fresh Wash Water
1.75 lb/lb coal
Washed Cake
58% Solids
Concentrated Spent Leachant
Enclosed Rotary Vacuum Disc Filters
Enclosed Horizonal Vacuum Belt Filter
Screen Bowl Centrifuge

FIGURE 10. **HTT COAL WASHING AND SEPARATION CIRCUIT**

TABLE 2.

CHEMICAL ANALYSIS OF RAW AND HYDROTHERMALLY DESULFURIZED PITTSBURGH SEAM (WESTLAND) COAL

	H_2O	Ash, MF[a]	S, MAF[b]	Na, MF	Ca, MF
Raw Coal, percent	2.11	7.96	2.08	0.02	0.07
Treated Coal, percent[c]	42.0	7.88	0.86	0.43	2.65

(a) MF: Moisture free basis.

(b) MAF: Moisture, ash free basis.

(c) Raw coal ground -50 mesh prior to treatment with 0.24 lb NaOH/lb coal and 0.10 lb CaO/lb coal at 275 C and 1000 psig. Washing conducted by six stages of saturated lime water repulp washing at a 2.0 lb wash water/lb dry solids ratio. Separation was by vacuum filtration followed by a final centrifuge dewatering.

SURVEY OF COALS TREATED BY OXYDESULFURIZATION

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ABSTRACT

The feasibility of using only compressed air and water at elevated temperature to reduce the sulfur content of coal has been demonstrated in autoclave experimentation at the Pittsburgh Energy Technology Center for various coals from most of the major coal basins in the United States. This air/water oxydesulfurization consistently removes in excess of 90 percent of the pyritic sulfur and has the potential for reducing the organic sulfur content by up to 40 percent. The sulfur liberated from coal by this reaction is present in the aqueous effluent as dilute sulfuric acid which can be neutralized with limestone. Under certain reaction conditions pyrite forms a jarosite intermediate which reports as organic sulfur in chemical analysis. Extent of organic sulfur removal and loss of heating value increase with temperature in the range 170°-200°C.

INTRODUCTION

Precombustion removal of sulfur and minerals from coal by physical/chemical cleaning is a developing technology that will provide alternate approaches to the electric utility industry and industrial boiler installations for complying with EPA New Source Performance Standards (NSPS) and future revisions without relying totally on flue gas desulfurization (FGD) (Friedman and Warzinski, 1977). These approaches could vary from physical/chemical cleaning alone to combining it with FGD. A combination approach could potentially reduce capital and operating costs by increasing reliability, reducing duplication of equipment needed to achieve present reliability, improving feedstock uniformity, reducing trace elements and ash constituents responsible for deposits and corrosion, and reducing sludge disposal problems. (Engdahl and Rosenberg, 1978; Balzhiser, 1978).

The only methods of coal cleaning practiced commercially are physical methods which utilize density differences and surface properties to achieve separation of coal and associated minerals. At an acceptable level of fuel value loss physical cleaning removes only accessible pyritic sulfur, leaving behind that which is finely divided throughout the coal matrix and sulfur chemically bound to the organic coal matrix. Therefore, only a small percentage of coals can be brought into compliance using only physical cleaning. On the other hand the selective chemical removal of sulfur from coal is capable of approaching complete pyritic sulfur elimination and, depending on the process, removal of the reactive organic forms of sulfur in coal.

A variety of chemical cleaning processes are under development and have been reviewed in the literature. (Friedman and Warzinski, 1977; Oder, et.al., 1977; Versar, Inc., 1978; Meyers, 1977). This report deals with the developmental research of one of these techniques, air/water oxidative desulfurization (termed Oxydesulfurization).

Air/water oxidative desulfurization has been demonstrated in autoclave experiments for various coals representative of the major U.S. coal basins (Friedman and Warzinski, 1977). The reaction proceeds most effectively at temperatures of 150 to 200° C at a total system pressure of 3.5 to 10.4 MPa (500 to 1500 psig). Above 200° C, coal and product heating value losses become substantial due to the oxidative loss of carbon and hydrogen. The pyritic sulfur solubilization reactions are typically complete (95 percent removal) within 15 to 40 minutes at temperature; however, significant organic sulfur removal requires residence times as long as 60 minutes at the higher temperatures. The principal products of the reaction are sulfuric acid and iron oxide. Several samples of coals treated by air/water oxidative desulfurization were exhaustively extracted with toluene which was then removed on a rotary evaporator. No elemental sulfur was detected.

Although little is known of the organic sulfur reactions (Friedman, LaCount and Warzinski, 1977), the pyrite/air oxidation reaction in aqueous media has been studied extensively by Vracar and Vucurovic (1970, 1971, 1972) in relation to producing sulfuric acid from pyrite for use in ore extraction. The following reactions were proposed for finely ground pyrite based upon conditions similar to those used for coal by Friedman and Warzinski (1977).

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (1)$$

$$2FeSO_4 + 1/2O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O \quad (2)$$

$$Fe_2(SO_4)_3 + nH_2O \rightarrow Fe_2O_3 \cdot (n-3)H_2O + 3H_2SO_4 \quad (3)$$

$$3Fe_2(SO_4)_3 + 14H_2O \rightarrow 2Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O + 5H_2SO_4 \quad (4)$$

Above 140° C no elemental sulfur was observed. Small amounts of the basic jarosite salt (reaction 4) were formed at lower pH and temperature. Vracar and Vucurovic (1972) observed that for a 20 gm/l pyrite slurry under the conditions 200° C, 0.61 to 1.02 MPa (74-133 psi) oxygen partial pressure, and 3 hour residence time, pyrite was completely converted to sulfuric acid and iron oxide. At temperatures below 200° C small amounts of unreacted pyrite, ferrous, and ferric sulfate were present. The pyrite reaction rate was found to be first order in unreacted pyrite with an activation energy of 51.0 kJ/mole (12.2 kcal/mole). In a more recent kinetic study, Slagle (1978), using an Upper Freeport coal under similar conditions, also found the pyritic sulfur reaction to be first order in unreacted pyrite with an activation energy of 46.7 k J/mole (11.2 k cal/mole). The organic sulfur data were scattered, but were fitted to a zero order rate expression with an activation energy of 78.7 k J/mole (18.8 k cal/mole). Broader reviews of pyrite oxidation and coal sulfur oxidation have been published by Meyers (1977) and Slagle (1978) covering reaction temperatures and pressures outside the ranges utilized for air/water oxydesulfurization.

EXPERIMENTAL

Air/water Oxydesulfurization coal screening experiments consist of treating a slurry of 35 gm of 200 x 0 mesh coal in 100 ml distilled water contained in a glass, teflon, or stainless steel liner inserted into a one liter, magnetically stirred, 316 stainless steel autoclave. The autoclave system can be operated in batch or semibatch modes. In the batch mode the autoclave containing the slurry is pressurized with air at room temperature to the desired oxygen partial pressure and subsequently heated by a jacket type heater to reaction temperature at a rate of approximately 3° C/minute. The slurry is agitated at 900 to 1000 RPM with a 3.175 cm diameter gas dispersion turbine-type impeller. Reaction temperature, once reached, is stabilized to within $\pm 2^{\circ}$ C by a proportioning temperature controller and manually operated internal water cooling coil. After the desired residence time at reaction temperature, the cooling coil is used to quench the reaction by lowering the temperature at a rate of approximately 50 to 60° C/minute. When the autoclave reaches room temperature a gas sample is taken and the product slurry removed.

The product slurry is filtered through Whatman 541 paper in a Buchner funnel and washed with distilled water until the pH of the filtrate tests 4 to 5 with litmus paper, normally requiring about one liter of distilled water. The product coal is extracted on a Soxhlet with distilled water until all soluble sulfates are removed, as determined with barium chloride. Analyses of the initial filtrate and Soxhlet washings indicate greater than 90 percent of the soluble sulfur compounds are removed from the product coal in the first wash. The coal sample is finally vacuum dried at 110° C for approximately 2 hours, weighed, and sent for analysis.

In the semibatch mode of operation a constant air flow in the range of 52 to 208 liters/hour (STP) is used to maintain constant system pressure and essentially constant oxygen partial pressure throughout the reaction. In order to minimize the evaporation and loss of water from the slurry, approximately 70 ml of distilled water is placed between the reactor wall and the liner while charging the autoclave to help saturate the effluent gas. The autoclave is purged with nitrogen at atmospheric pressure, closed off, and heated to reaction temperature. When this temperature is attained the autoclave is rapidly pressurized with air to the desired operating pressure and the continuous air flow started. The reaction is quenched by terminating the air flow and using the internal cooling coil. Gas samples are normally taken during and at completion of the reaction. The product workup is identical to that of the batch mode.

RESULTS AND DISCUSSION

Twenty-four coals have been treated by air/water oxidative desulfurization. Data for sulfur removal are given in Table 1, and the balance of the ultimate analyses are in Table 2. All twenty-four coals, unless noted in Table 1, were treated for one hour at the temperature indicated under either 5.6 MPa (800 psig) initial air pressure in the batch mode or 7.0 MPa (1000 psig) total system pressure in the semibatch mode. An air flow of approximately 200 liters/hour (STP) was used in the semibatch mode. The mode of operation is also indicated in Table 1. The first ten coals in the two tables would meet the current EPA NSPS of 1.2 lb SO_2 per 10^6 BTU. Due to retention of sulfurous products in the ash during combustion, coals containing somewhat greater than 0.6 lb S per 10^6 BTU can be expected to meet NSPS (EPA, 1977). Reflecting the greater effectiveness of Oxydesulfurization for removing more pyritic than organic sulfur, all ten of the untreated coals had less than one percent organic sulfur.

Coals 11-17 in the two tables had moderate amounts of organic sulfur, up to 1.5 percent. Depending on the sulfur-retention properties of the ash, some of these coals might meet NSPS. Relatively small improvements in Oxydesulfurization processing could also bring these coals into compliance.

Coals 18-24 in the two tables had high organic sulfur contents, greater than 1.5 percent. For these coals significant improvement in organic sulfur removal would be necessary to bring them into compliance. However, due to their high organic sulfur contents, these coals have been used to

Weight Percent (Moisture Free)

#	Coal Seam	Mine	State	ASTM Rank	Total Sulfur		Pyritic Sulfur		Organic Sulfur		BTU/lb (Dry)		Recovery (%)	lbsS/MM BTU		Reaction Temperature (°C)
					Untr[8]	Tr[9]	Untr	Tr	Untr	Tr	Untr	Tr		Untr	Tr	
1	Black Creek	Natural Bridge Strip	AL	Mvb	1.22	0.65	0.42	0.16	0.69	0.47	13595	11694	94	0.90	0.56	180[5]
2	1	Peacock	CO	HvBb	1.88	0.67	0.95	0.10	0.60	0.57	13123	11001	92	1.45	0.61	200[5]
3	Imboden	Paramount Elkhorn No. 1 Strip	VA	HvAb	1.19	0.95	0.26	0.04	0.78	0.79	14273	13977	100	0.83	0.61	150[5]
4	Lower Freeport	Luciusboro Strip	PA	HvAb	2.83	0.75	2.03	0.02	0.65	0.68	12775	11944	99	2.22	0.63	180[5]
5	Lower Kittanning	2	PA	LvB	0.96	0.57	0.53	0.08	0.39	0.47	14590	13630	98	0.66	0.42	150
6	Middle Kittanning	Congo Strip	OH	HvCb	1.08	0.60	0.26	0.04	0.78	0.55	11184	9648	89	0.96	0.62	180[5]
7	Mammoth	Storm King	MT	SbA	0.83	0.57	0.32	0.18	0.45	0.36	11770	10910	92	0.70	0.52	150
8	Pittsburgh	Bruceton	PA	HvAb	1.31	0.80	0.61	0.05	0.68	0.71	14170	13430	100	0.92	0.60	150
9	Upper Freeport	Laker	MD	Mvb	1.58	0.54	0.82	0.02	0.56	0.50	12642	11117	99	1.25	0.48	200[5]
10	Upper Freeport	Coal Junction Strip	PA	Mvb	2.14	0.63	1.37	0.04	0.49	0.50	11256	10213	95	1.90	0.62	200[5]
11	Brookville	Humphrey	PA	HvAb	4.20	1.17	3.06	0.13	1.11	1.01	13250	11346	96	3.17	1.03	180
12	Lower Freeport	West Valley Strip	PA	HvAb	4.14	1.04	3.09	0.22	1.01	0.78	13112	11395	98	3.15	0.91	180
13	Pittsburgh	Pitkulski Strip	PA	HvAb	1.67	0.89	0.71	0.03	0.82	0.83	11650	10890	100	1.43	0.81	160
14	Pittsburgh	No. 43 Strip	OH	HvAb	3.88	1.05	2.36	0.19	1.48	0.84	12657	10780	98	3.06	0.97	180
15	Pittsburgh	No. 43 Strip	OH	HvBb	3.01	0.98	1.93	0.16	1.05	0.80	12846	10787	98	2.34	0.90	180
16	Whitebrest	Lovilia No. 4	IA	HvCb	5.85	1.07	3.95	0.18	0.90	0.76	10870	9140	81	5.38	1.17	150[6]
17	Wyoming No. 9	Reliance	WY	HvCb	1.75	0.90	0.38	0.06	1.14	0.82	12410	11480	101	1.41	0.78	150
18	Bevier	No. 22 Strip	KS	HvAb	5.00	1.98	2.92	0.36	2.04	1.60	12203	12224	93	4.10	1.62	150
19	Illinois No. 5	3	IL	HvCb	3.34	2.03	0.92	0.12	2.06	1.82	12650	11600	90	2.64	1.75	150
20	Illinois No. 6	River King	IL	HvBb	3.69	2.12	1.13	0.11	2.25	2.00	12190	10030	89	3.03	2.11	150[7]
21	Indiana No. 5	Enos	IN	HvBb	3.27	1.84	0.70	0.20	1.98	1.64	12340	10095	91	2.65	1.82	250[7]
22	4	Homestead	KY	HvAb	4.80	2.34	1.08	0.12	2.33	2.14	11380	11250	93	4.22	2.08	160
23	Minshall	Chrisney No. 1	IN	HvBb	5.65	1.43	3.01	0.10	1.53	1.22	11320	10230	85	4.99	1.40	200
24	Pittsburgh	Ireland	WV	HvAb	3.89	2.09	1.38	0.02	2.18	2.03	13390	12190	99	2.90	1.71	180

1. Uncorrelated Coal Seam 2. Obtained from Cambria Slope Preparation Plant 3. Information Not Available
4. Blend of Kentucky Seams No. 9, No. 11, No. 13 5. Modified Semicontinuous Mode (8→9 SCFH Air Flow) All others batch flow.
6. Four repressurizations in batch mode. 7. 1500 psig Initial Air in batch mode. 8 Untreated 9. Treated

Table I. - Summary of Coals Treated By Air/Water Oxydesulfurization

Moisture Free-Weight Percent

Coal[1]	Ash		Carbon		Hydrogen		Nitrogen		Oxygen	
	Untr[2]	Tr[3]	Untr	Tr	Untr	Tr	Untr	Tr	Untr	Tr
1	3.7	2.6	76.9	71.6	5.2	3.8	1.6	1.6	11.4	19.8
2	6.5	5.2	73.7	68.0	5.3	3.6	1.6	1.9	10.9	20.5
3	3.7	3.4	80.2	79.6	5.1	4.9	1.5	1.4	8.4	9.9
4	15.1	13.3	72.5	70.2	4.5	3.9	1.3	1.3	3.7	10.6
5	7.1	7.0	83.5	79.8	4.4	4.1	1.4	1.4	2.6	7.2
6	16.9	15.3	64.6	59.6	4.4	3.4	1.2	1.1	11.8	20.0
7	9.5	7.5	68.4	66.4	4.5	4.0	1.2	1.2	15.6	20.4
8	5.5	4.6	79.4	76.5	5.3	4.8	1.5	1.5	7.0	11.7
9	16.2	14.6	72.3	67.7	4.3	3.3	1.3	1.2	4.3	12.7
10	22.4	21.4	65.0	62.0	3.6	3.0	1.1	1.2	5.9	11.8
11	9.3	6.6	73.3	68.2	5.2	3.9	1.7	1.4	6.3	18.7
12	11.7	8.8	73.5	68.2	4.9	3.7	1.3	1.2	4.5	17.0
13	21.4	20.1	65.4	63.0	4.4	3.9	1.3	1.3	5.9	10.7
14	12.7	10.4	70.7	66.1	4.8	3.8	1.6	1.4	6.4	17.2
15	11.2	9.3	72.1	66.1	4.8	3.6	1.8	1.3	7.0	18.7
16	17.4	16.4	63.0	56.3	4.2	3.3	1.2	1.1	8.3	21.9
17	3.2	2.1	72.4	69.2	4.7	4.2	1.6	1.5	16.4	22.0
18	14.8	12.0	68.6	69.3	4.8	4.7	1.1	1.2	5.7	10.8
19	8.7	6.6	70.8	68.2	5.0	4.3	1.4	1.4	10.7	17.6
20	11.6	11.0	68.4	61.0	4.6	3.4	1.2	1.1	10.6	21.2
21	9.1	11.5	69.4	63.4	4.9	3.1	1.6	1.5	11.8	18.7
22	14.1	11.4	63.8	65.4	4.6	4.2	1.3	1.4	11.3	15.3
23	15.9	11.1	62.8	63.2	4.6	3.3	1.2	1.3	9.8	19.7
24	7.8	6.8	73.4	71.0	5.1	4.5	1.3	1.2	8.5	14.4

[1] See table 1. [2] Untreated [3] Treated

Table 2. - Summary of Coals Treated by Air/Water Oxydesulfurization

investigate the removal of organic sulfur by air/water oxidative desulfurization.

With increasing severity of operating conditions, increasing amounts of organic sulfur can be removed. However, the organic sulfur removal is accompanied by heating value losses for the coal. This is not surprising, since one would expect oxidation of organic structures to proceed at a rate at least comparable to that for oxidation and cleavage of some C-S bonds. An organic sulfur removal efficiency may be defined as the ratio of the differential increase in organic sulfur removal to the differential increase in heating value loss. So defined, this efficiency is equal to the slope of a line describing data as plotted in Figure 1. The data, from Table 1, exhibit considerable scatter. It should be remembered that, besides temperature variations, the data also represent coals of six different ranks, ranging from hvAb to sbA. Slagle and Shah (1978) prepared a similar plot for a single coal with variable temperature and observed a linear correlation superior to that shown in Figure 1.

The data in Figure 1 and those of Slagle and Shah (1978) were both for a single top size of coal, 200 mesh. Wheelock et. al. (1978) have presented data from which plots such as Figure 1 may be constructed for top sizes of 200 and 400 mesh. Such plots reveal a higher organic sulfur removal efficiency for the larger top size of coal. This finding suggests a surface effect. In the absence of such an effect the smaller particles would be expected to exhibit a higher

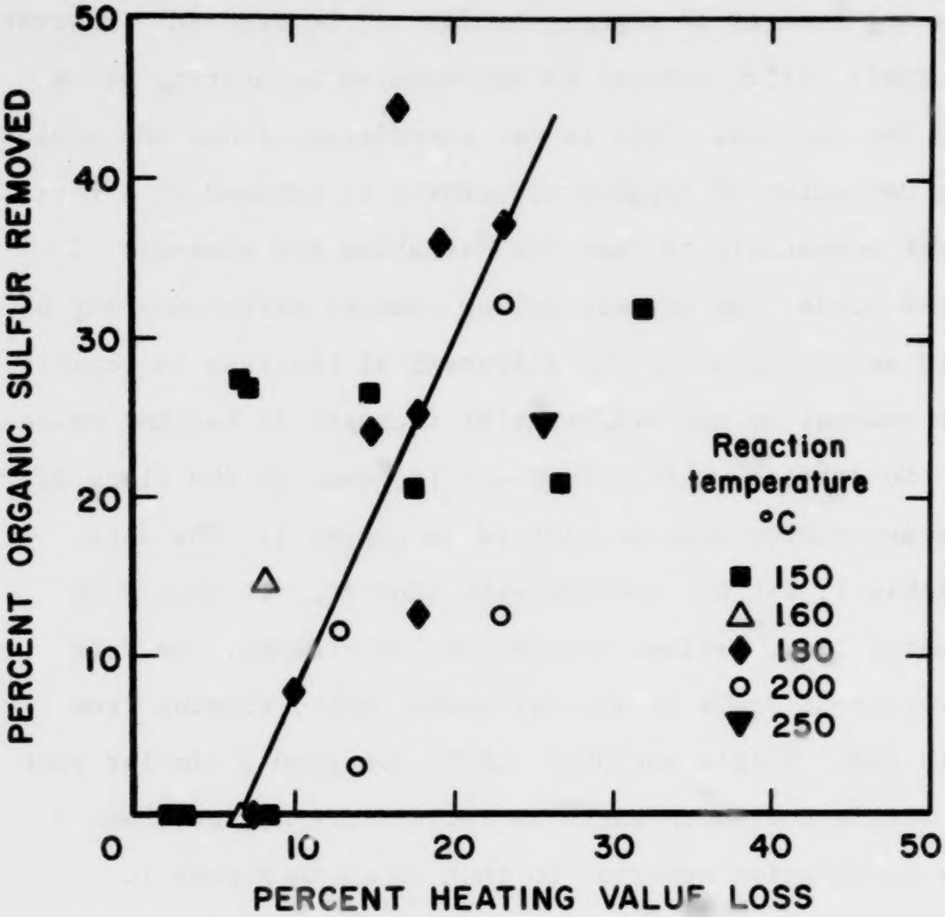

Figure I-Organic sulfur removal efficiency.

organic sulfur removal efficiency, since the leachant would have access to a larger fraction of all sulfur contained in the coal (Medieros and Peterson, 1976).

The data in Table 2 show an increase in oxygen content of coal due to processing. This effect is shown graphically in Figure 2, where moles of oxygen taken up by the coal per mole of carbon in the product coal is seen to increase with loss of heating value. Hydrogen and carbon in the coal decrease due to processing. The data in Table 2 are plotted in Figure 3. It is seen, for the range of heating value loss encountered, between zero and 30 percent, that hydrogen is preferentially removed from the organic matrix. Apparently heating value is lost both by consumption of the coal to final oxidation products, carbon dioxide and water, and by partial replacement of hydrogen by oxygen in the coal.

A beneficial side benefit of Oxydesulfurization treatment is reduction in the ash content of the coal. Part of the ash probably is dissolved in the sulfuric acid formed during reaction. Inspection of Table 2 shows a maximum ash reduction of 41 percent and an average reduction for all coals treated of 20 percent.

An interesting effect that has been observed with some coals is an apparent increase in organic sulfur with oxidative desulfurization treatment. An example is shown in Figure 4. The four experiments shown were made on a Lower Freeport coal according to the standard procedure for the continuous air feed mode, using the reaction conditions listed. Over 95

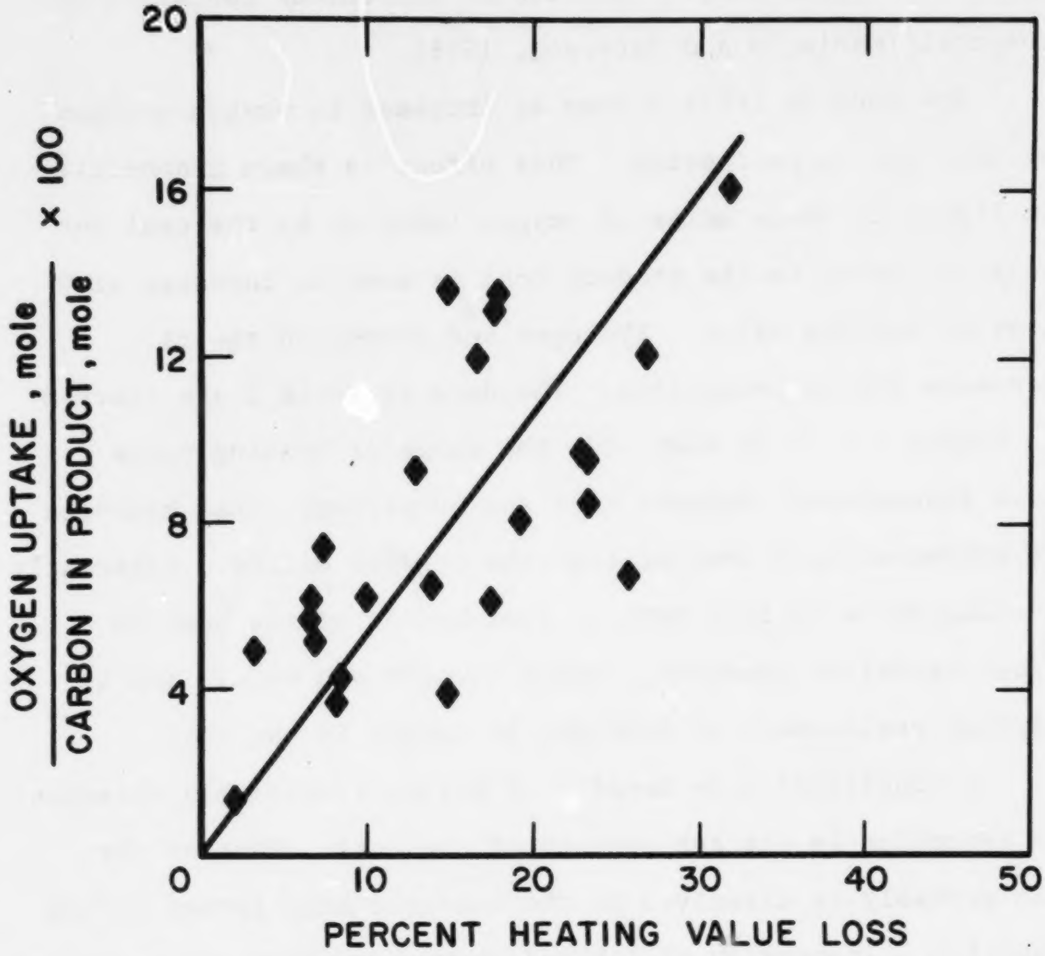

Figure 2-Oxygen uptake by coal due to treatment.

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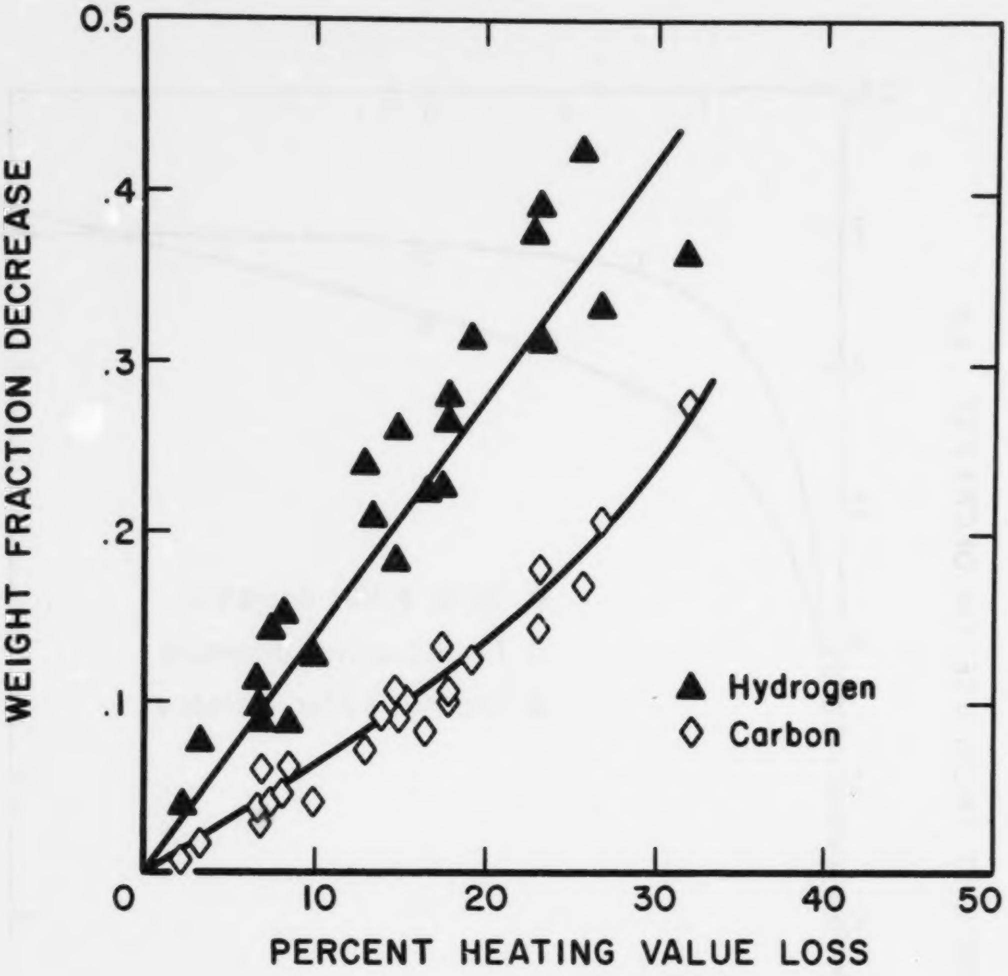

Figure 3 - Carbon and hydrogen loss due to treatment .

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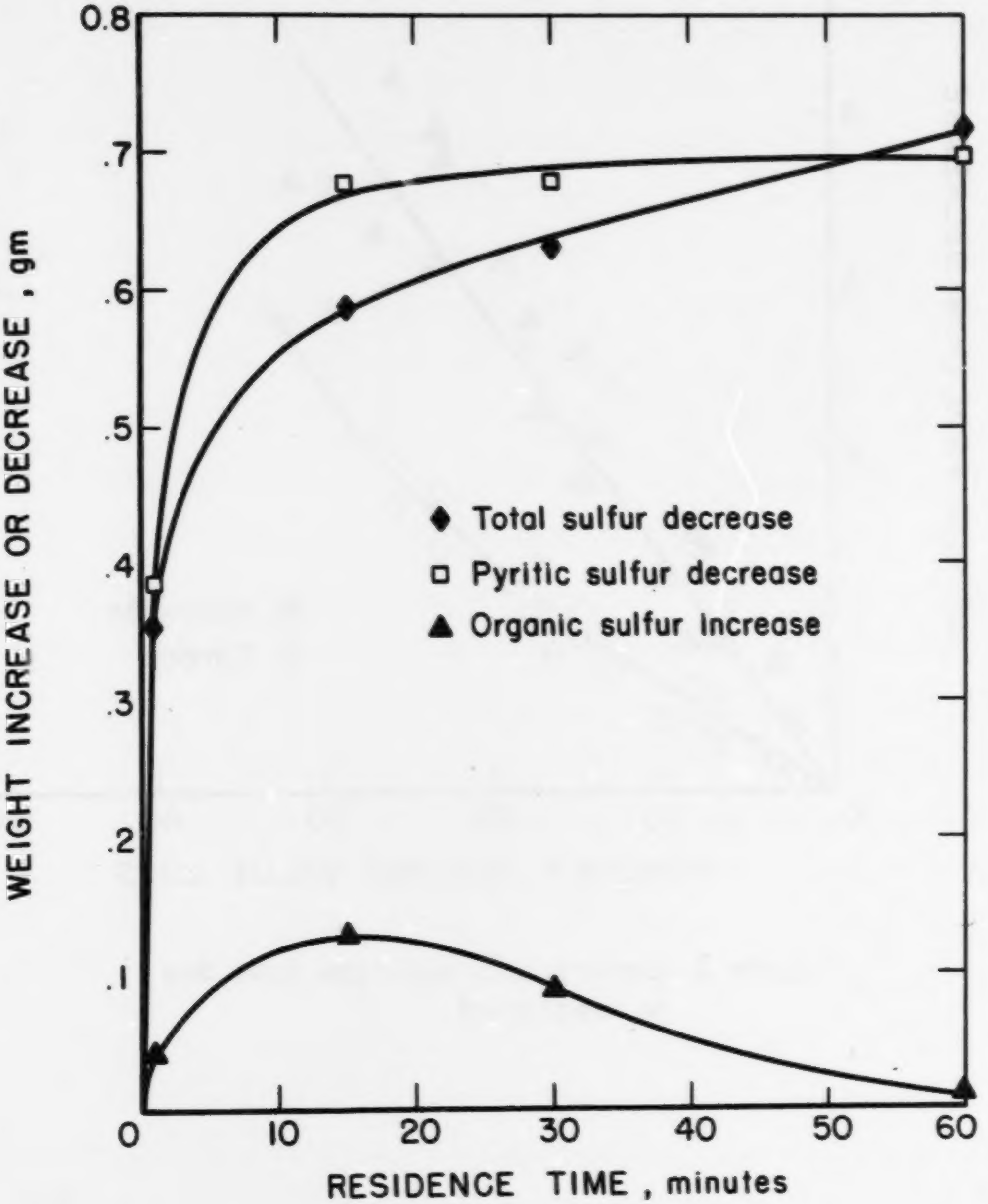

Figure 4-Apparent increase in organic sulfur with treatment. (Lower Freeport HVAb, 180°C, 1000 psig air, 35 g coal charge).

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percent of the pyritic sulfur is removed in the first 15 minutes, resulting in a total sulfur decrease of 60 percent. The organic sulfur registers an apparent increase, however, with the peak value at 15 minutes being 55 percent larger than the value for the untreated coal. With longer treat time the apparent organic sulfur decreases again, the value at one hour being close to the value for the untreated coal.

We do not believe that organic sulfur is created during processing, but rather that the anomalous results are an artifact arising from the analytical determination of organic sulfur by difference. The formation of jarosite-like basic salts is well known in hydrometallurgy. One such species is shown in Equation (4), as suggested by Vracar and Vukurovic (1970). Other solids can also be formed in our system, containing as it does ferrous, ferric, and sulfate ions, and smaller concentrations of other cations. Kwok and Robins (1973) have reviewed the formation of so-called thermal precipitates in aqueous solutions. Some of their data showing the formation of thermal precipitates in aqueous ferrous and ferric sulfate solutions are shown in Figure 5. For solutions with ferrous or ferric concentrations as indicated by a particular curve, a precipitate forms when the temperature and pH at 25° C place the system to the right of the curve. From calculated concentrations of ferrous/ferric ions and measured values of pH, we determine that the formation of thermal precipitates is possible in our system.

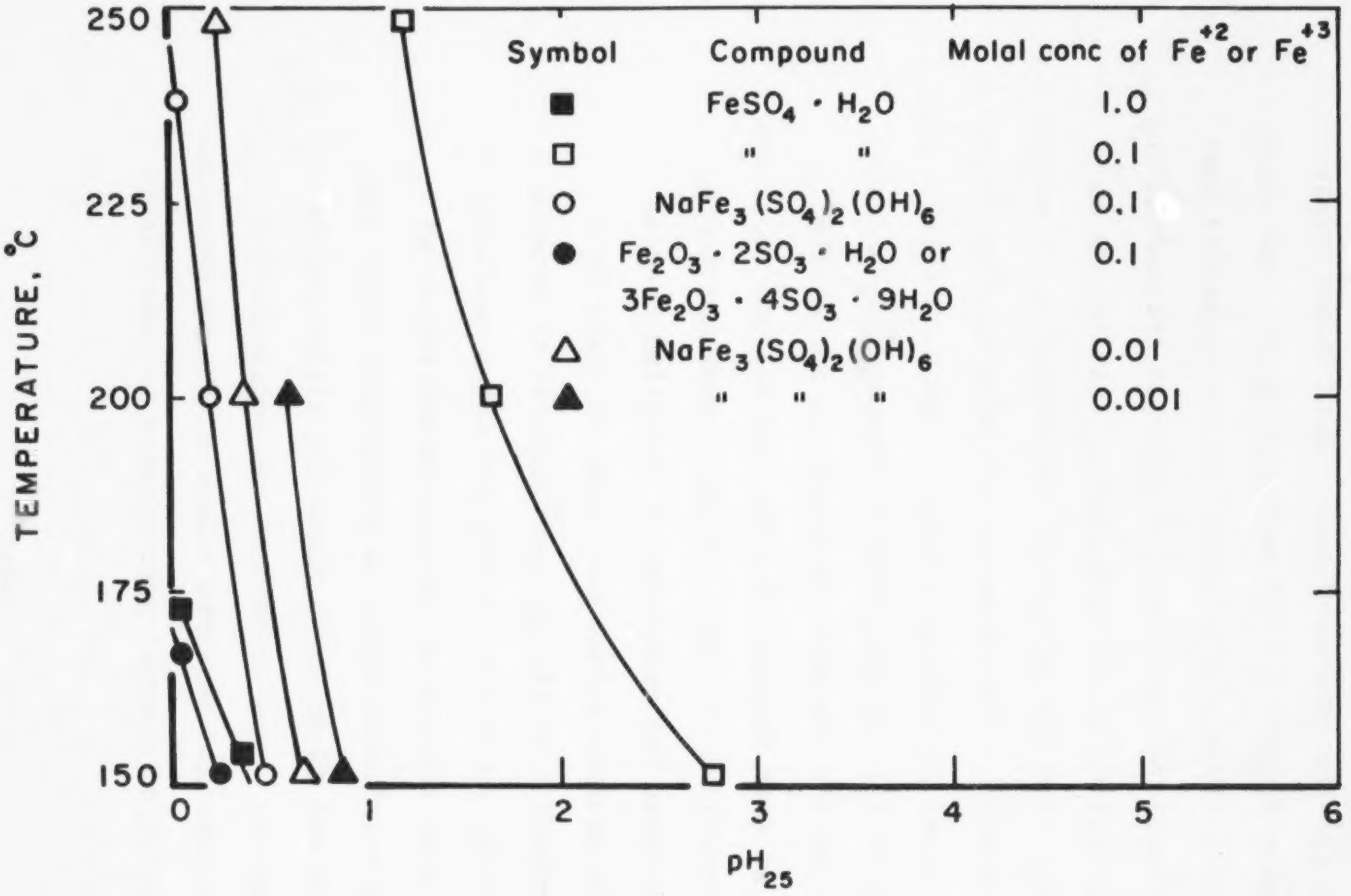

Figure 5 – Thermal precipitation of iron compounds in $H_2SO_4-H_2O$ (Na_2SO_4) system.

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We believe an explanation for Figure 4 is that jarosite-like compounds are formed in the early stages of reaction in which the pyrite is nearly completely consumed. The jarosites are not the most thermodynamically stable species at reaction conditions, but may form due to localized fluctuations in solution concentration in the vicinity of pyrite crystallites at the time they go into solution. Kept in contact with the leachant solution the jarosites digest to more stable forms, ferric oxide and sulfuric acid, which do not contain sulfur in the solid phase.

A thermal precipitate was formed in an experiment in which a model sulfur compound was subjected to Oxydesulfurization process conditions. X-ray diffraction analysis indicated that the precipitate was jarosite-like. X-ray fluorescence showed the major components of the precipitate to be iron and sulfur. No sodium was detected by this method or by atomic absorption. Therefore, the compound is not natrojarosite, for which the equilibrium precipitation temperature/acidity diagram is shown in Figure 5, but rather the basic sulfate as proposed by Vracar and Vucurovic (1970) in Equation (4). Analysis of precipitate by a Fisher sulfur analyzer indicated a sulfur content of 13.4 percent, which is close to the theoretical value of 13.34 percent for $Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O$.

To test the possibility that jarosite-like compounds are responsible for apparent organic sulfur increase, a sample of an Upper Freeport seam coal was doped with the collected jarosite-like precipitate and submitted for analysis.

All of the sulfur in the doped coal, including the jarosite sulfur, was determined by the ASTM Eschka method, but only 86 percent of jarosite sulfur was reported as sulfate sulfur. None was reported as pyrite; the 14 percent balance, therefore, reported as organic sulfur. The organic sulfur in the doped sample, as a result, was 37 percent higher than normal.

TOWARDS A COMMERCIAL OXYDESULFURIZATION PROCESS

Work is continuing at the Pittsburgh Energy Technology Center to move chemical coal cleaning to a commercial reality. To this end a continuous reactor has been built and operated within the past months to conduct air/water oxidative desulfurization. A slurry bubble column reactor is employed, consisting of a vertical tube 2.22 cm inside diameter by 183 cm long. Preheated air and aqueous coal slurry are fed to the reactor cocurrently at the bottom. The treated coal slurry and exit gas are removed at the top.

Operation of the continuous reactor to date has been encouraging. Using an Upper Freeport coal (number 4 in Tables 1 and 2) at conditions of temperature and pressure as established in the autoclave work, some results were as follows. For a slurry space time of 6 minutes, the weight percent total sulfur was reduced from 1.82 in the feed coal to 0.87 in the product coal. With a slurry space time of 69 minutes the weight percent total sulfur in the product was 0.70. Slurry space time is defined as reactor volume divided by volumetric slurry feed rate.

A more complete account of operations with the continuous reactor will be made at a later time. Our experience to date however, has enabled us to develop a conceptual flow sheet for an Oxydesulfurization process. It is shown in Figure 6. The flow sheet can be considered in three sections: coal preparation, reaction and coal recovery, and acid neutralization.

In the coal preparation section run of mine coal is subjected to a number of conventional physical coal cleaning operations to remove white rock and some separable pyrite. These cleaning operations employ a grizzly, rotary breaker, and jig plant. The physically cleaned coal is stored in a day bin before being sent to a ring mill and ball mills for grinding. The ground coal is slurried, preheated, and fed to a slurry bubble column reactor. Also fed to the reactor is compressed air. Spent air/ steam from the reactor is used in a turbine expander to supply some of the power required for air compression. Product coal from the reactor is filtered, dried, and is then ready for use.

Effluent water from the reactor, containing sulfuric acid, is neutralized. Shown on the flowsheet are steps for the grinding and storage of limestone. The acid water and limestone are combined in the neutralization tank. By-product gypsum is removed by filtration, and the treated water is recycled to the slurry preparation tank.

The flow sheet illustrates the complementarity of physical and chemical coal cleaning methods. Relatively

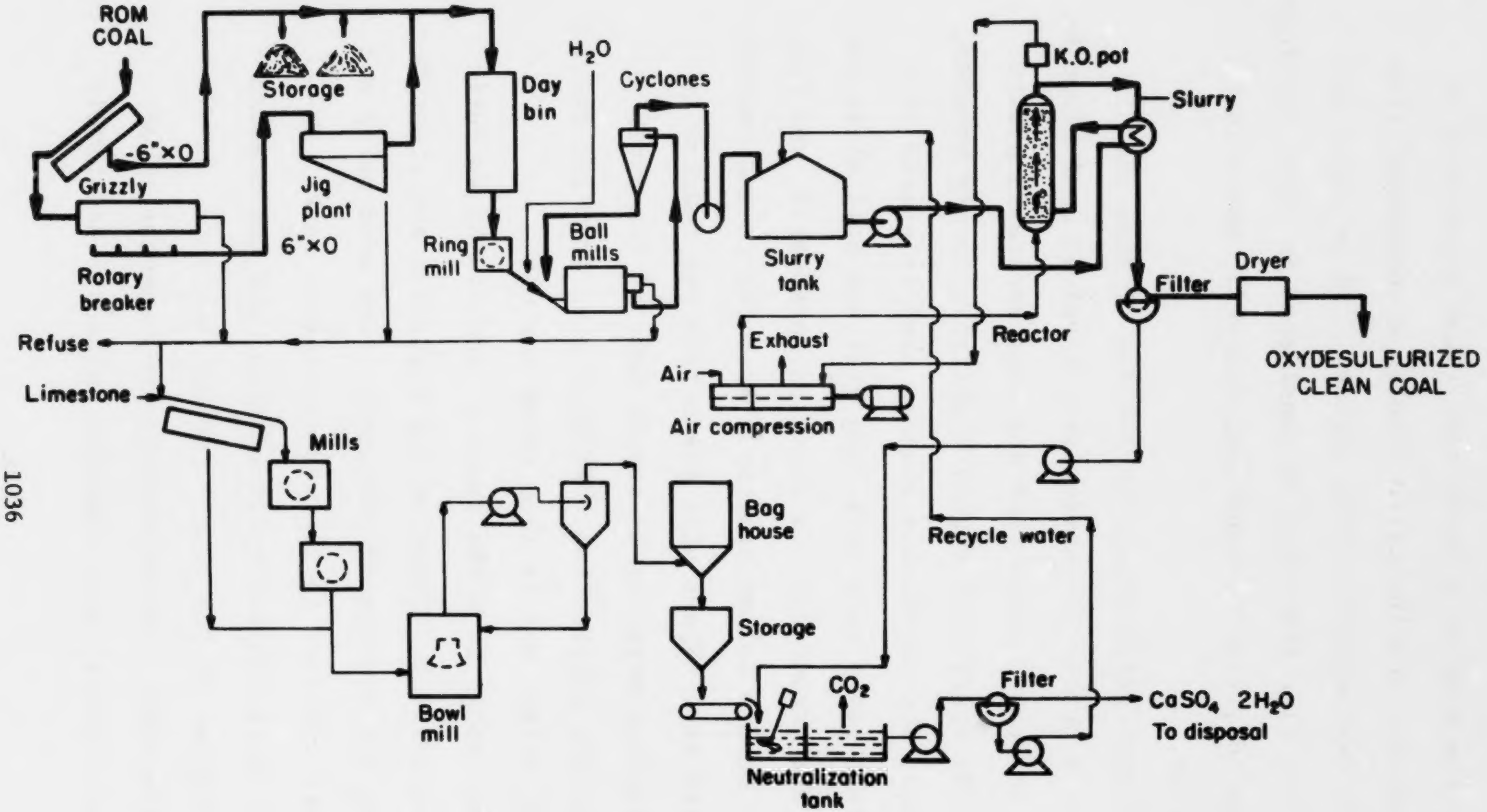

Figure 6 - Oxydesulfurization process

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more washable coals would have a higher fraction of sulfur removed in the physical preparation section; those less washable would have a more sulfur removed by chemical cleaning. Also apparent is the simplicity of the process. Air, water, and limestone are the only materials required to treat the coal.

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COAL DESULFURIZATION BY LEACHING WITH ALKALINE SOLUTIONS CONTAINING OXYGEN

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ABSTRACT

Hot alkaline solutions containing dissolved oxygen under pressure were used to leach sulfur from bituminous coals in a small, stirred autoclave. The reduction of sulfur content in coal was studied as a function of the stirring rate, leaching time, temperature, pressure, and concentration of alkali. Under relatively mild conditions, almost all of the inorganic sulfur and a significant portion of the organic sulfur were removed. Dilute alkaline solutions were more effective than acidic solutions in the removal of organic and inorganic sulfur, but the heating value recovery was somewhat higher for acidic solutions. Also, oxygen was shown to be more effective than air as the oxidizing medium. Under alkaline conditions, more organic sulfur was removed when the oxygen partial pressure was increased. Optimum values were determined for the concentration of alkali and for the temperature of the leaching process, under given conditions.

INTRODUCTION

Chemical methods for the removal of sulfur from coal have received wide attention (Friedman and Warzinski, 1977; Meyers, 1977; Wheelock, 1977; Wheelock, 1978). Among the more promising are processes based on extraction of sulfur by leaching with aqueous solutions containing dissolved oxygen (Agarwal et al., 1975; Friedman et al., 1977; Tai et al., 1977). The rate of extraction can be increased by operating at elevated temperature and pressure. Although generally the leaching solutions are acidic, either initially or as a result of the generation of sulfuric acid during the oxidation of pyritic sulfur, basic solutions containing ammonia have also been proposed (Agarwal et al., 1976; Sareen, 1977). Apparently, the use of basic solutions allows a significant extraction of the organic sulfur as well as the pyritic sulfur from coal under milder conditions. The leaching temperatures for basic solutions are relatively low, generally less than 150°C. The advantages of using alkaline conditions for leaching high-sulfur coals were also demonstrated by Tai et al.(1977).

A unique chemical desulfurization (oxydesulfurization) process is being developed at the Ames Laboratory, Iowa State

University, which is based on leaching fine-size coal with a hot, dilute sodium carbonate solution containing dissolved oxygen under pressure (Wheelock et al., 1978). In this process, sulfur is extracted from coal by conversion into soluble sulfates. For pyrite the overall conversion reaction appears to be:

$$2\ FeS_2 + 7.5\ O_2 + 4\ H_2O = Fe_2O_3 + 4\ H_2SO_4.$$

The pyritic iron remains as an insoluble iron oxide or hematite (Chen, 1978). The sulfuric acid generated in the process is immediately neutralized by the alkali as follows:

$$H_2SO_4 + Na_2CO_3 = Na_2SO_4 + CO_2 + H_2O.$$

The mechanism for the extraction of a portion of the organic sulfur has not been established.

In this work, several high-sulfur bituminous coals were leached under various conditions. The effects of important parameters such as agitation, leaching time, temperature, oxygen partial pressure, and alkalinity on the process were studied. The results will be used to optimize the oxydesulfurization process.

EXPERIMENTAL

Apparatus

The leaching experiments were conducted in a 1-liter stirred autoclave reactor (Autoclave Engineers, Inc., Model AFP 1005) made of Type 316 stainless steel. The reactor was furnished with a removable, protective liner made of stainless steel, an electric heating jacket, a proportional temperature controller, an internal cooling coil, and a pressure gauge.

The contents of the autoclave was stirred by a gas-dispersing turbine agitator operated by a magnetic drive.

Procedure

For each experiment, the autoclave reactor was charged with 40 g. of coal plus 400 ml. of the leach solution and sealed. The desired agitator speed was established,and the autoclave was purged with nitrogen gas while being heated up to temperature. When the desired temperature was reached, the flow of nitrogen was stopped, the autoclave was vented, and oxygen was introduced into the autoclave. The oxygen partial pressure (psia), the total pressure within the autoclave (psig), the temperature, and the stirrring rate were kept constant for the duration of the experiment. Some gas was bled continuously from the reactor to prevent any build-up of gaseous reaction products, while the system pressure was kept constant by supplying oxygen on demand. At the end of a run, the flow of oxygen was stopped, the system purged with nitrogen, and the reactor cooled. The leached coal was then recovered by filtration, dried at 90°C for 1 day, weighed, and analyzed for the various forms of sulfur, ash content, and heating value by standard ASTM procedures.

Materials

Three of the coals used for leaching came from mines located in southeastern Iowa (Lovilia mine, Big Ben mine, and Scott coal from the Iowa State University demonstration mine). Another was a Western Kentucky coal (No.9 seam) from the Fies Mine in Hopkins Co., KY. The Iowa coals were high-volatile bituminous coals, high in sulfur content, and very heterogeneous in composition. The coals were dried at 90°C for 1 day, ground and sieved to the desired mesh size, and analyzed prior to leaching.

Calculations

The heating value recovery, in percent, was calculated by the following equation:

$$\text{Recovery } (\%) = \frac{(\text{wt. coal recovered}) \times \text{heating value} \times 100}{(\text{wt. coal started}) \times \text{heating value}}$$

The specific sulfur content ($\text{lb.S}/10^6$ Btu), used in the tabular data, was calculated as follows:

$$\text{Specific sulfur content} = \frac{\text{percent sulfur} \times 10^6}{100 \times \text{heating value (in Btu/lb.)}}$$

There is a slight difference in the two forms in which the data are presented. In the tables, the percent of sulfur reduction is based on changes in the specific sulfur content ($\text{lb.S}/10^6$ Btu); in the graphs, it is based on the change in the weight percent of sulfur.

RESULTS AND DISCUSSION

Effect of stirring rate

In order to establish the effect of the stirring rate of the turbine agitator on the amount of sulfur removed from coal by leaching, Scott coal was leached for 1 hr. by 0.2$\underline{M}$ sodium carbonate at 150°C and 50 psia oxygen partial pressure. The results are presented graphically in Figure 1. The amount of pyritic and total sulfur extracted from coal increased steadily as the rotation speed was increased from 200 to 1200 r.p.m. Between 1200 and 1400 r.p.m., the amount of sulfur extracted (both pyritic and total sulfur) increased sharply. For agitator speeds above 1400 r.p.m., the amount of pyritic and total sulfur removed began to level off and approached a constant value between 1800 and 2100 r.p.m., being about 90 and 63% for pyritic and total sulfur, respectively. Within this range, the amount of extracted sulfur was independent of the agitator speed, indicating that the rate of extraction was no longer limited by the mass transfer of oxygen through the solution surrounding the individual particles.

A similar dependency on stirring rate was observed by Kosikov et al.(1973) during their study of the oxidation of pyrite by air in an autoclave. In their explanation, the effect of stirring is due to the amount of oxygen dissolved in the solution. With increased agitation, the amount of dissolved oxygen increases until it reaches a limiting value determined by Henry's law.

The study of the effect of agitator speed on the amount of sulfur extracted was repeated at a higher oxygen partial pressure, i.e. 200 psia. The data shown in Figure 2 indicate that above 800 r.p.m.the reduction in total sulfur content increased more steeply and then leveled off sooner, at about 1200 r.p.m., and at a higher sulfur reduction value, approximately 67%, than at the lower oxygen partial pressure of 50 psia. The reason for the steeper rise in sulfur removal may be higher solubility of oxygen in the alkaline leach solution at

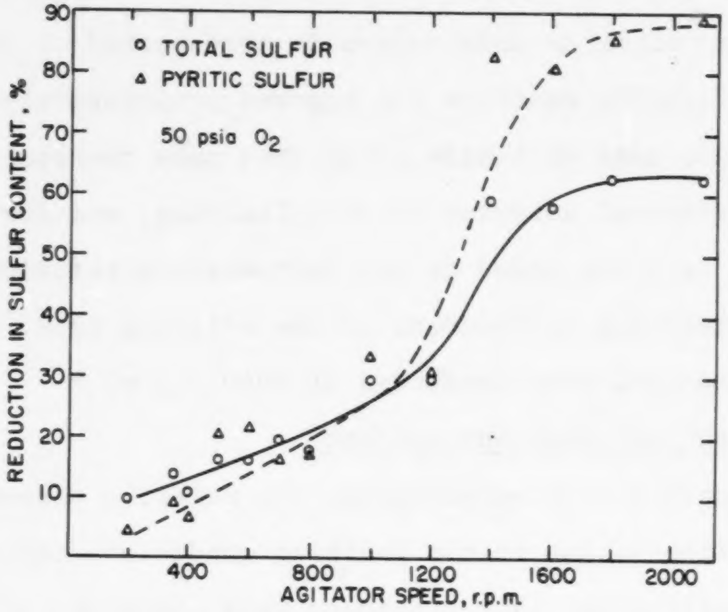

Figure 1. Effect of agitator speed on the removal of sulfur from coal for 50 psia oxygen partial pressure.

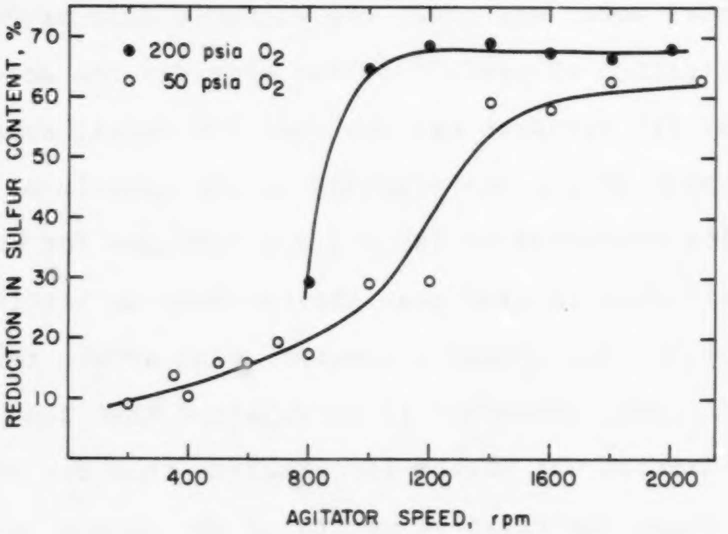

Figure 2. The interaction of agitator speed and oxygen partial pressure on total sulfur removal.

higher pressure. Thus, with increased stirring rate the mass transport is higher for the solution with the greater oxygen concentration; as more oxygen is transported to the particle surface, the reaction can proceed progressively faster. At the plateau, some mechanism other than mass transport through the external solution is rate-limiting, and further increases in rotation speed do not increase the reaction rate. To keep the leaching independent of the stirring rate, all further experiments were conducted at 2000 r.p.m.

Effect of leach solution and oxidant

In the next set of experiments, the relative effectiveness of alkaline versus acidic leaching conditions and of pure oxygen versus air as the oxidant were compared. The four run-of-mine coals, -200 mesh, were leached for 1 hr. at 150°C and 50 psia oxygen partial pressure. Under alkaline conditions, 0.2M sodium carbonate was the leaching solution. For acidic conditions, pure water was used; the sulfuric acid produced during the oxidation of pyritic sulfur provided the acidity. The oxygen partial pressure was the same (50 psia), regardless of whether oxygen or air was supplied to the autoclave.

The results presented in Table 1 are averages for duplicate runs. Although in each case the recovery in heating value was high, it was slightly greater under acidic than under alkaline conditions. However, it is apparent that the percentage sulfur reduction was higher for alkaline than for acidic conditions. Since the relative merits of air versus oxygen are more difficult to discern, the data were subjected to statistical analysis.

Table 1. Leaching of coals (-200 mesh) with water and with alkali using air or pure oxygen.[a]

Gas Type	H.V. Btu/lb.	Ash wt.%	lb.S/10^6 Btu				Tot. S Redn. %	H.V. Recov. %
			Pyr.	Sulf.	Org.	Tot.		
	10,050[b]	20.7	3.08	1.07	0.97	5.12	(Lovilia Coal)	
O_2	10,320	17.1	0.92	0.51	1.15	2.58	49.6	95.3
Air	10,260	17.7	1.66	0.64	0.91	3.21	37.3	94.7
O_2[c]	9,520	23.5	0.56	0.22	0.71	1.49	70.9	86.9
Air[c]	9,420	23.6	1.11	0.22	0.85	2.18	57.4	88.3
	10,530[b]	15.0	3.50	1.52	1.67	6.69	(Big Ben Coal)	
O_2	11,003	11.3	1.18	0.38	1.66	3.22	51.9	97.1
Air	10,860	12.5	2.58	0.34	1.41	4.33	35.3	92.8
O_2[c]	10,260	17.3	0.72	0.34	0.97	2.03	69.7	88.2
Air[c]	10,140	18.3	0.81	0.32	1.02	2.15	67.9	86.3
	10,270[b]	16.9	6.24	1.86	2.53	10.63	(Scott Coal)	
O_2	11,260	12.4	1.42	0.34	3.21	4.97	53.2	93.9
Air	11,050	14.1	4.15	0.20	2.72	7.07	33.5	95.6
O_2[c]	10,520	18.2	1.93	0.22	1.94	4.09	61.5	93.2
Air[c]	10,340	19.6	2.78	0.30	1.85	4.93	53.6	91.7
	10,890[b]	18.3	0.89	0.86	1.43	3.18	(West. Ky. Coal)	
O_2	10,930	16.6	0.10	0.37	1.53	2.00	37.1	95.7
Air	11,180	16.3	0.13	0.33	1.63	2.09	34.3	95.7
O_2[c]	10,240	21.8	0.08	0.09	1.31	1.48	53.5	89.2
Air[c]	10,730	20.6	0.09	0.10	1.37	1.56	50.9	92.9

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[a] Leached 1 hr. at 150°C and 50 psia O_2 partial pressure.

[b] Heating value, ash content, and sulfur distribution of unleached coal.

[c] Leach solution was 0.2M sodium carbonate.

The general conclusion drawn from the statistical analysis is that the nature of the leaching solution (alkaline or acidic) has a greater effect on desulfurization than the nature of the oxidant (air or oxygen). Specifically, desulfurization is more effective, at the 99.5% confidence level, under alkaline than under acidic conditions. Also, at a slightly lower confidence level, namely 95%, oxygen can be said to be a better oxidant than air.

Closer scrutiny of the data in Table 1 reveals also that in almost every case both the pyritic and the organic sulfur contents were significantly lower for alkaline than for acidic leaching conditions. Use of air versus oxygen, however, produced no discernible difference in the organic sulfur content. For the pyritic sulfur content, use of oxygen tended to result in lower values than use of air.

The relative effectiveness of alkaline, neutral, and acidic conditions under various oxygen partial pressures will also be discussed further below.

Effect of leaching time

The effect of leaching time on the desulfurization of Lovilia coal is presented in Table 2 and in Figure 3. At 150°C and 50 psia oxygen partial pressure, prolonged leaching with 0.2M sodium carbonate improved the extraction of sulfur at first. But after about 1.5 hr., the reduction in total sulfur leveled off at about 76-79%. The initial increase in extraction seemed due to the removal of additional pyritic sulfur, since the amount of organic sulfur removed appeared fairly constant

Table 2. Oxydesulfurization of coal as a function of leaching time.[a]

Time hr.	H.V. Btu/lb.	Ash %	lb.S/10^6 Btu Pyr.	Sulf.	Org.	Tot.	Tot. S Redn. %	H.V. Recov. %
0	10,175[b]	18.6	3.84	0.92	1.02	5.78	-	-
0.5	9,686	22.5	0.92	0.24	0.67	1.83	68.3	86.9
1.0	9,601	23.2	0.76	0.15	0.87	1.78	69.2	86.1
1.5	9,674	22.6	0.56	0.25	0.55	1.36	76.5	81.3
2.0	9,706	22.4	0.39	0.22	0.74	1.35	76.6	81.6
2.5	9,414	24.7	1.03	0.34	0.70	2.07	64.2	76.6
3.0	9,651	22.8	0.53	0.22	0.48	1.23	78.7	80.9

[a] Lovilia coal (-200/+250 mesh), leached with 0.2M Na_2CO_3 at 150°C and 50 psia O_2.

[b] Heating value, ash content, and sulfur distribution of unleached coal.

(from an initial 1.02 lb.S/10^6 Btu down to an average of 0.67 lb. S/10^6 Btu). At the same time, the heating value recovery decreased with increasing leaching time. Thus, the small advantage in removal of some additional pyritic sulfur was offset by a higher loss in heating value.

Effect of oxygen partial pressure

The beneficial effect of increased oxygen partial pressure on the desulfurization of coal has already been observed in Figure 2. A set of experiments was then designed to study this effect over the range of 25-200 psia oxygen partial pressure by leaching Lovilia and Western Kentucky coals with 0.2M sodium carbonate at 150°C. From the results shown in Table 3 and in

Table 3. Effect of oxygen partial pressure on alkaline leaching of Lovilia coal (-200/+250 mesh).[a]

O_2 Press. psia	H.V. Btu/lb.	Ash %	lb.S/10^6 Btu Pyr.	Sulf.	Org.	Tot.	Tot. S Redn. %	H.V. Recov. %
-	10,175[b]	18.6	3.84	0.92	1.02	5.78	-	-
25	9,522	23.9	0.78	0.22	0.91	1.91	67.0	86.6
50	9,600	23.2	0.76	0.15	0.87	1.78	69.2	86.1
75	9,588	23.3	0.57	0.23	0.78	1.58	72.7	86.2
100	9,619	23.1	0.57	0.25	0.83	1.65	71.5	86.3
125	9,449	24.4	0.93	0.22	0.93	2.08	64.0	86.2
150	9,716	22.3	0.34	0.22	0.76	1.32	77.2	86.9
175	9,676	22.6	0.40	0.26	0.69	1.35	76.6	87.0
200	9,618	23.1	0.36	0.23	0.78	1.37	76.3	84.1

[a] Leached 1 hr. with 0.2$\underline{M}$ Na_2CO_3 at 150°C.

[b] Heating value, ash content, and sulfur distribution of unleached coal.

Figure 4, it is evident that the reduction in the total sulfur of Lovilia coal increased from 67% up to 76-77% by increasing the oxygen partial pressure. The slight improvement can be attributed to additional removal of both pyritic and organic sulfur. By contrast, the improved desulfurization of Western Kentucky coal with increasing oxygen partial pressure was due to the increased removal of organic sulfur and not pyritic sulfur (data shown in Table 4 and Figure 5). There is no ready explanation for this difference in the behavior of the pyritic sulfur of the two coals. Lovilia coal seems also unique in that

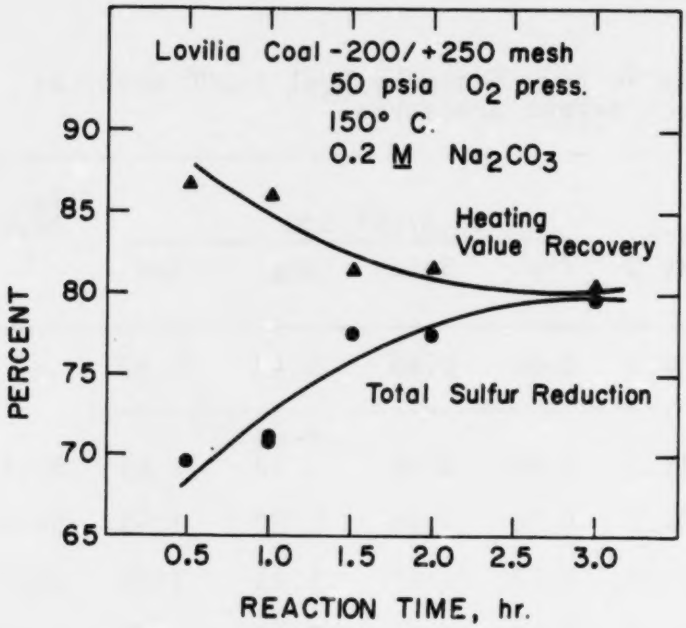

Figure 3. Effect of leaching time on oxydesulfurization of coal.

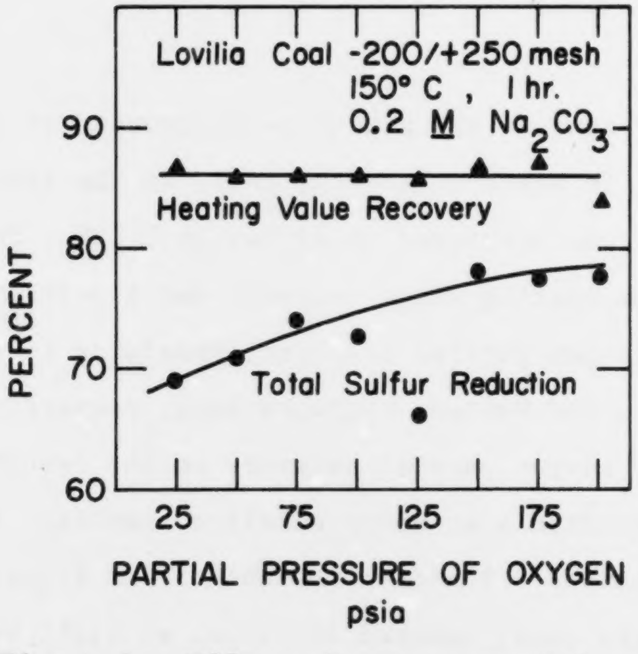

Figure 4. Effect of oxygen partial pressure on oxydesulfurization of coal.

Table 4. Leaching Western Kentucky Coal (-200 mesh) at different oxygen pressures.[a]

O_2 Press psia	H.V. Btu/lb.	Ash wt.%	lb.S/10^6 Btu				Tot. S Redn. %	H.V. Recov. %
			Pyr.	Sulf.	Org.	Tot.		
	10,890[b]	18.3	0.89	0.86	1.43	3.18	--	--
50	10,237	21.8	0.08	0.09	1.32	1.49	53.3	89.2
100	10,370	21.9	0.16	0.08	1.22	1.45	54.6	89.4
150	10,375	21.9	0.17	0.09	1.15	1.41	55.9	89.5
200	10,383	21.8	0.13	0.14	1.12	1.38	56.5	90.2

[a] Leached 1 hr. by 0.2M Na_2CO_3 at 150°C. Data are averages of duplicate runs.

[b] Heating value, ash content, and sulfur distribution of unleached coal.

the pyritic sulfur content was almost never reduced to a level below about 0.4%. In Western Kentucky coal, on the other hand, the pyritic sulfur was decreased to as low as 0.13%. For both coals, however, the heating value recovery was almost unaffected by the increased oxygen partial pressure, remaining at about 86 and 90% for Lovilia and Western Kentucky coal, respectively.

The effect of oxygen partial pressure on the desulfurization of coal was studied also under alkaline, neutral, and acidic leaching conditions. The data in Table 5 and Figure 6 are for Western Kentucky coal, leached for 1 hr. at 150°C by 0.2M sodium carbonate, 0.2N sulfuric acid, or water at pressures from 50 to 200 psia oxygen.

Table 5. Effect of oxygen partial pressure on the leaching of coal with alkaline,neutral or acidic solutions[a].

O_2 Press psia	H.V. Btu/lb.	Ash %	lb.S/10^6 Btu				Tot. S Redn. %	H.V. Recov. %
			Pyr.	Sulf.	Org.	Tot.		
	10,890[b]	18.3	0.89	0.86	1.43	3.18	---	---
0.2M Na_2CO_3								
50	10,322	21.7	0.10	0.07	1.32	1.49	53.1	90.0
100	10,368	21.9	0.15	0.07	1.21	1.43	55.0	87.8
150	10,344	22.1	0.20	0.09	1.13	1.42	55.3	86.9
200	10,230	22.9	0.13	0.13	1.19	1.45	54.4	90.2
water[c]								
50	10,885	16.8	0.12	0.28	1.49	1.89	40.6	97.2
100	10,090	16.4	0.13	0.27	1.41	1.81	43.1	95.0
150	11,138	16.1	0.16	0.22	1.29	1.67	47.5	96.7
200	11,148	16.0	0.14	0.20	1.27	1.61	49.4	96.2
0.2N H_2SO_4								
100	11,212	15.5	0.10	0.44	1.41	1.95	36.7	98.5
150	11,204	15.6	0.11	0.38	1.34	1.83	42.4	95.9
200	11,185	15.7	0.11	0.43	1.31	1.85	41.8	96.8

[a] Western Kentucky coal (-200 mesh), leached 1 hr. at 150°C.

[b] Heating value, ash content, and sulfur distribution of uncleachd coal.

[c] Initial solution, becomes acidic as leaching proceeds.

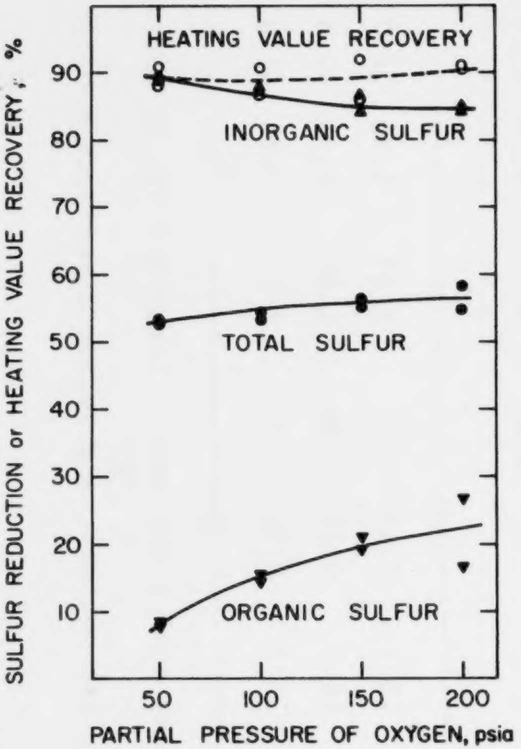

Figure 5. Effect of oxygen partial pressure on leaching of Western Kentucky coal.

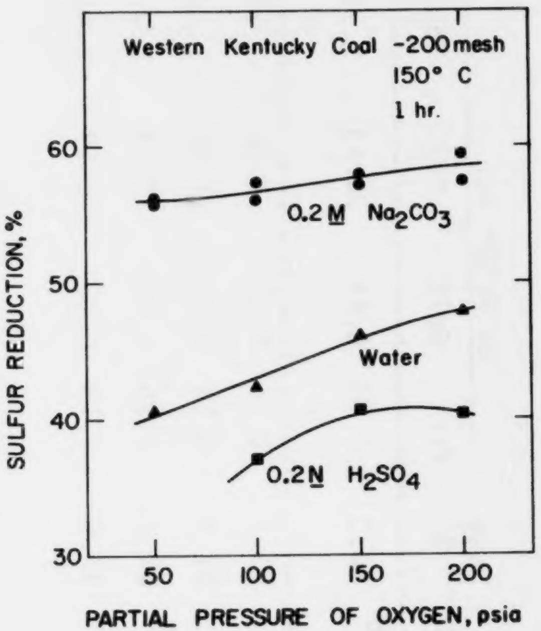

Figure 6. Effect of oxygen partial pressure on oxydesulfurization of coal by leaching with alkaline, neutral or acidic solutions.

When water was used as the leachant, the initially neutral solution became acidic during the leaching process because of the production of sulfuric acid. Under these conditions, the reduction of total sulfur increased almost linearly with increasing oxygen pressure, from 40.6% at 50 psia to 49.4% at 200 psia oxygen partial pressure. When the leachant was initially acidic (0.2N sulfuric acid), the reduction of total sulfur was less favorable, ranging from 36.7% at 100 psia, through 42.4% at 150 psia, to 41.8% at 200 psia oxygen partial pressure.

When 0.2M sodium carbonate was the leachant, the total sulfur reduction was much higher; however, it seemed to increase only slightly with increasing oxygen partial pressure, from 53.1 to 55.3%. The amount of organic sulfur in the leached residue was less than that for the other leachants and appeared to decrease with increasing pressure. The heating value recovery, on the other hand, was lower under alkaline conditions (87-90%) than under acidic conditions (96-99%).

It should be noted that none of the coal samples removed from the autoclave were washed with water after the leaching treatment. This obviously had an effect on the residual levels of sulfate in the leached coal, amounting to about 0.2 lb.S/10^6 Btu. In the case of sulfuric acid as the leachant, this effect was even more noticeable with residual sulfate levels of about 0.4 lb. S/10^6 Btu. In addition to improving the total sulfur reduction, a washing step would also decrease the ash content of the leached coal. The benefits of washing leached coal by water or by dilute acid were recognized by Tai et al. (1977).

Effect of alkali concentration

The data in Table 6 and Figure 7 show the effect of the alkali concentration on the desulfurization of Lovilia coal at 150°C and 50 psia oxygen partial pressure for 1 hr. With no sodium carbonate present in the leach solution, the reduction of total sulfur was 58%. The presence of even a small amount of alkali, i.e. 0.05M sodium carbonate, improved the total sulfur reduction significantly, to 66%. Further increases in alkali concentration resulted in only slight improvement, while at higher concentrations the reduction of total sulfur even declined. The optimum concentration seemed to be 0.15-0.2M sodium carbonate, resulting in approximately 71% reduction of total sulfur. For this same concentration range, the residual amounts of pyritic, sulfate, and organic sulfur appeared to be minimum. Higher concentrations of alkali were also detrimental to the heating value recovery, causing a decline from 92.7 to 78.9% in the recovery by increasing the sodium carbonate concentration from 0.05 to 0.5M. Even worse heating value recoveries were observed at higher alkali concentrations (Wheelock et al., 1978).

Effect of temperature

The results of the effect of the leaching temperature on the desulfurization of Lovilia coal are presented in Table 7 and Figure 8. With increasing temperature, the total sulfur reduction increased at first, then passed through a broad maximum, after which it decreased at an accelerating rate. The optimum temperature range was approximately 120-150° C; up to 71.4%

Table 6. Effect of sodium carbonate concentration on leaching of coal.[a]

Conc. Na_2CO_3 M	H.V. Btu/lb.	Ash %	lb.S/10^6 Btu				Tot.S Redn. %	H.V. Recov. %
			Pyr.	Sulf.	Org.	Tot.		
--	10,418[b]	18.0	3.24	0.90	0.99	5.13	--	--
0[c]	10,982	13.4	1.08	0.29	0.80	2.17	58.0	91.7
0.05	10,833	14.1	0.68	0.36	0.71	1.75	66.2	92.7
0.10[d]	10,401	17.9	0.73	0.24	0.72	1.69	67.4	89.2
1.15[d]	10,156	19.9	0.62	0.20	0.71	1.53	70.5	88.2
0.20[d]	9,858	22.2	0.82	0.21	0.81	1.84	64.4	86.7
0.25	9,680	23.6	1.14	0.22	0.93	2.29	55.7	86.2
0.30[d]	9,340	25.8	0.82	0.28	0.86	1.96	61.7	84.4
0.40[d]	9,246	26.5	0.74	0.21	0.84	1.99	61.2	80.2
0.50[d]	9,186	27.0	0.70	0.46	0.80	1.96	61.9	78.9

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[a] Lovilia coal (-200/+250 mesh), leached 1 hr. at 150°C and 50 psia O_2.

[b] Heating value, ash content, and sulfur distribution of unleached coal.

[c] Leach solution was initially water; became acidic as leaching proceeded.

[d] Values are averages of duplicate runs.

Table 7. Effect of temperature on the leaching of coal with alkali.[a]

Temp. °C	H.V. Btu/lb.	Ash %	lb.S/10^6 Btu				Tot.S Redn. %	H.V. Recov. %
			Pyr.	Sulf.	Org.	Tot.		
--	10,047[b]	19.6	3.90	0.94	0.93	5.77	--	--
100	9,666	22.6	1.25	0.28	0.69	2.22	61.5	89.7
120	9,634	22.9	0.80	0.29	0.56	1.65	71.4	88.2
130	9,662	22.7	0.88	0.23	0.64	1.75	69.7	89.2
150[c]	9,268	25.9	1.42	0.20	0.70	2.32	59.9	83.6
170	9,205	26.3	1.51	0.27	0.59	2.37	58.9	80.2
180[c]	9,016	27.8	1.71	0.22	0.98	2.91	49.7	75.9
200	8,950	28.4	2.69	0.23	0.98	3.90	32.4	78.2
--	10,390[b]	18.3	3.12	0.94	1.03	5.09	--	--
110[d]	9,783	23.1	0.59	0.25	0.89	1.73	66.0	90.2

[a] Lovilia coal (-200/+250 mesh), leached 1 hr. with 0.2M Na_2CO_3 at 50 psia O_2.

[b] Heating value, ash content, and sulfur distribution of unleached coal.

[c] Average of duplicate runs.

[d] Control sample for this run was sample immediately above.

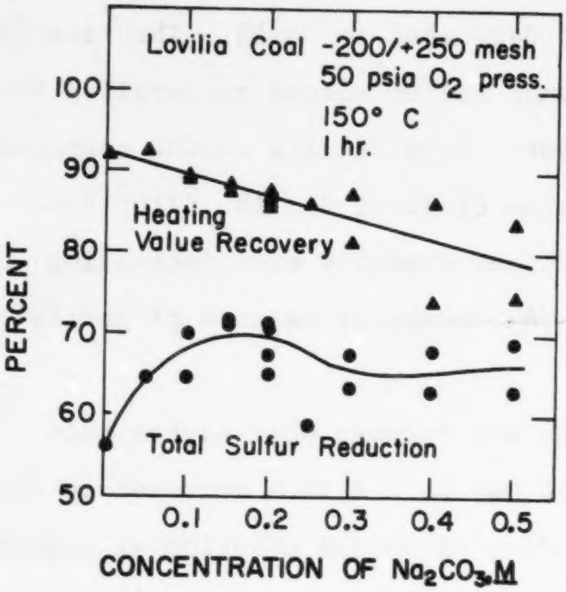

Figure 7. Effect of sodium carbonate concentration on oxydesulfurization of coal.

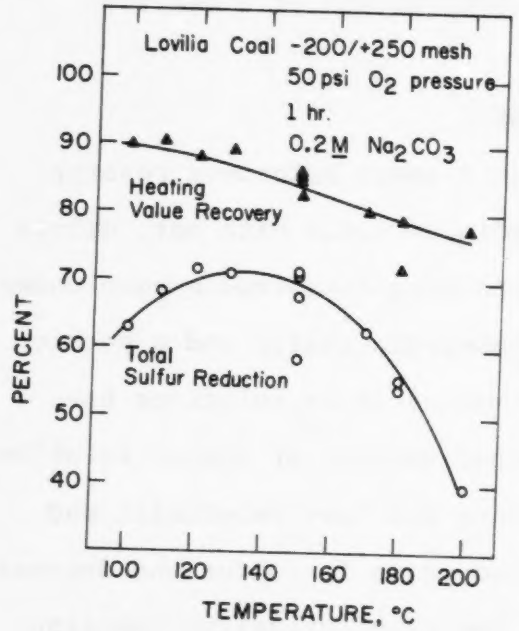

Figure 8. Oxydesulfurization of coal as a function of temperature.

of the total sulfur was extracted in this region. At 200 °C, the total sulfur reduction had decreased to 32.4%. The relative reductions in pyritic and organic sulfur seemed to parallel the reduction curve for total sulfur. Only sulfate sulfur appeared to have a constant residual value of about 0.2 lb. S/10^6 Btu. The heating value recovery declined steadily with increasing temperature, from 90% down to 78%, probably because of partial oxidation of coal.

At the present time, it is not certain what causes this unusual temperature effect. It may be due to a decrease in the solubility of oxygen in the sodium carbonate solution at higher temperatures. Or perhaps it may be caused by a thermally induced change in the structure of coal itself. Alternatively, there may be a change in the reaction mechanism or kinetics, possibly caused by the thermal decomposition of a reactive intermediate.

CONCLUSIONS

It has been demonstrated with a small autoclave reactor that leaching of high-sulfur bituminous coals with hot, dilute solutions of sodium carbonate containing dissolved oxygen under pressure can remove most of the inorganic sulfur and a portion of the organic sulfur. Dilute alkaline leach solutions have been shown to be more effective than neutral or acidic solutions. More concentrated alkaline solutions are less beneficial and even detrimental, causing lower reduction in sulfur and decreasing the heating value recovery. The desulfurization reaction becomes independent of the stirring rate at high stirring speeds.

Leaching longer than 1-1.5 hr. results only in a modest increase in sulfur removal, but the advantage is offset by a decrease in heating value recovery. Increasing the oxygen partial pressure improves the extraction of sulfur without a noticeable decrease in the heating value recovery. The improvement is due mainly to an increase in the removal of organic sulfur, amounting to 30% in some cases. An optimum temperature range has been observed at about 120-150°C for which the reduction of sulfur is maximum. At higher temperatures, both the extraction of sulfur and the heating value recovery decline significantly.

The overall Ames oxydesulfurization process has been shown to be effective in removing almost all of the inorganic sulfur and a significant portion of the organic sulfur under relatively mild conditions. The moderate temperatures and pressures do not require extraordinary equipment, and the alkaline conditions provide a non-corrosive environment. With proper regeneration of the leaching solution, the process should prove an economical method for the chemical cleaning of high-sulfur coal.

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CONVERSION TABLE TO INTERNATIONAL (SI) SYSTEM UNITS

1 Btu = 1,055 joules

1 lb. = 453.6 g

1 Btu/lb. = 2.324 joules/g

1 psi = 6.89 kPa

1 r.p.m. = 0.105 rad/sec

THE POTENTIAL FOR CHEMICAL COAL CLEANING: RESERVES, TECHNOLOGY, AND ECONOMICS

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ABSTRACT

Based on statistical data on U.S. bituminous coal reserves published by the U.S. Bureau of Mines, an estimate is presented on the tonnage of coal, by coal-producing region, which can potentially be made to conform to the New Source Performance Standard (NSPS) of 1.2 lb SO_2 per million Btu by chemically removing 90-95 percent of the pyritic sulfur and 0-40 percent of the organic sulfur.

The additional tonnage of conforming coal potentially obtainable by blending chemically cleaned coal with raw coal is estimated.

The impact of other criteria presently under discussion (0.2 lb SO_2 per million Btu; removal of 80-90 percent of the original sulfur) is presented on the tonnage of coal potentially made conforming by chemical cleaning.

The state of the art of chemical cleaning is summarized. Kennecott's laboratory data on the removal of pyritic and organic sulfur are discussed, and comparisons are made between: oxygen-water versus oxygen-ammonia leaching; low-temperature (130°C) versus high-temperature (175-200°C) leaching.

Technical data resulting from these comparisons are used to project capital and operating costs for grass-roots chemical coal cleaning plants. The economics of chemical coal cleaning are compared against the purchase of low-sulfur washed coal or the installation of scrubbers.

Introduction

Chemical coal cleaning studies were begun in 1971 by Kennecott Copper Corporation in an attempt to develop low sulfur coals from its Peabody Coal Company division's reserves. Analyses reported in 1974 (Agarwal et al., 1974) showed significant economic, energy conservation, and environmental advantages associated with chemical coal cleaning when compared with other coal conversion/desulfurization alternatives. An active coal desulfurization program was pursued by Kennecott until May 1975, when all coal research and development for Peabody Coal was terminated, because at that time the Supreme Court upheld the Federal Trade Commission ruling ordering Kennecott to divest itself of Peabody Coal. At termination, the development program had progressed to a stage at which batch testing was close to completion, and the main emphasis was on planning an internally funded pilot plant program. Results of the batch simulation of the leach reactors have mostly been reported in the literature by Sareen et al. (1975), and by Sareen (1977). In addition to leaching, every other major unit operation on the flowsheet had been batch-tested: separation and washing of clean coal from the leach reactor effluent, solution neutralization and separation of the gypsum thus formed, evaluation of materials of construction, etc. A detailed process design had shown that only conventional equipment would be required for a commercial plant, thus eliminating the need to develop new equipment for which there is no reliable scale-up experience.

The process is covered by U.S. patent 3,960,513 (Agarwal, Giberti, Petrovic, June 1976) assigned to Kennecott.

Since 1975 there have been, and will continue to be, changes in the laws regulating the sulfur content in coal, and in the economics of coal desulfurization/conversion processes. Kennecott has continued to update the economics of its chemical coal cleaning process, and to identify the reserves where it can be economically applied.

This paper will briefly summarize the experimental results, with particular emphasis on comparing some process alternatives; in addition, it will present recent reserve estimates, and provide updated economics.

General Considerations of Chemical Coal Cleaning

The removal of sulfur from coals by chemical leaching depends on the conversion of the various forms of sulfur to soluble species. Chemical leaching has two significant advantages over physical coal cleaning:

1. Fine, dispersed pyrite is removed from coals without excessive grinding.
2. Organic sulfur may be removed as well as pyrite.

Because sulfur exists in coal in three general forms, the separation of each form requires different chemistry:

1. Pyritic sulfur must be oxidized, either to sulfur or, preferably, to soluble sulfate. A variety of

oxidants, including air, tonnage oxygen, chlorine, etc., can achieve this.

2. Organic sulfur can be extracted by hydrogenation; part of the organic sulfur can also be converted to soluble sulfur species by oxidation.
3. Sulfates are generally soluble in aqueous solutions, hence do not require chemistry other than leaching.

Experimental Results

It is virtually impossible to make a sound technical and economic comparison of the various chemical leaching processes from published data, because the processes have been tested by different investigators with various coals and under varying conditions. This paper compares three oxygen leaching alternatives tested by Kennecott:

Low-temperature ($\leq 130^{\circ}C$)	coal/water slurry
Low-temperature ($\leq 130^{\circ}C$)	coal/aqueous ammonia slurry
High-temperature ($> 130^{\circ}C$)	coal/water slurry

Data have been previously reported for the low-temperature O_2/H_2O system (Sareen et al., 1975) and for the low-temperature O_2/NH_3 system (Sareen, 1977). Data on the high-temperature O_2/H_2O have not been reported heretofore.

Figure 1 shows the removal of pyritic sulfur from coal. At the identical temperature ($130^{\circ}C$), the rate of pyrite leaching for the O_2/NH_3 alternative is slightly lower than that for O_2/H_2O. It should be noted that no tests were run for short reaction times to establish the kinetics for the high tempera-

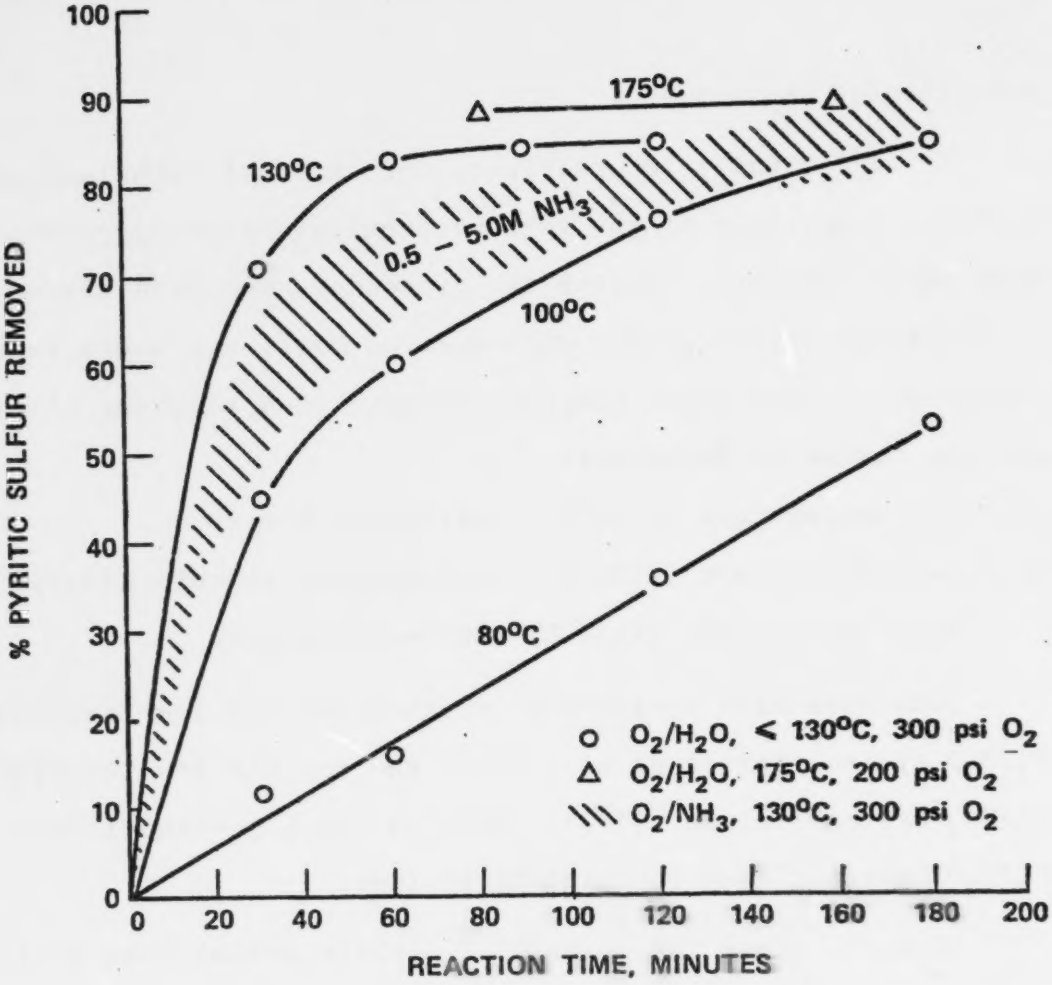

Figure 1. Pyrite Removal for Various Oxydesulfurization Conditions

ture (175°C) O_2/H_2O case. It should also be noted that the high temperature O_2/H_2O tests were run at 200 psi O_2 partial pressure rather than 300 psi, and that the rate of pyrite leaching has been reported (Sareen et al., 1975) to vary directly with the square root of the O_2 partial pressure.

The data for the O_2/NH_3 system are reported as a band for the five ammonia molarities tested (0.5, 1.04, 1.94, 2.95, 5.0) to simplify the comparison. All data were obtained with Illinois #6 coal.

Figure 2 shows the previously reported data for organic sulfur removal for the low temperature O_2/H_2O and O_2/NH_3 systems. Also shown are previously unreported data demonstrating the removal of organic sulfur at higher temperatures (175°C) in the O_2/H_2O system. Organic sulfur removal at the higher temperature is comparable to that in the O_2/NH_3 system. However, as shown in Figure 3, this is achieved at the expense of greater Btu losses. Figure 3 also shows the O_2/NH_3 system to have greater Btu losses than the O_2/H_2O system at the same temperature (130°C).

Data on the other process parameters, such as oxygen uptake by coal, extent of coal converted to CO_2, CO, and hydrocarbons, can mostly be found in the cited papers.

These data for Illinois #6 coal demonstrate the effect of leaching chemistry on the removal of pyrite and organic sulfur and the yield of heating value. Previously reported data indicate that comparable pyrite leaching behavior can be expected for other coal types. However, considerably different

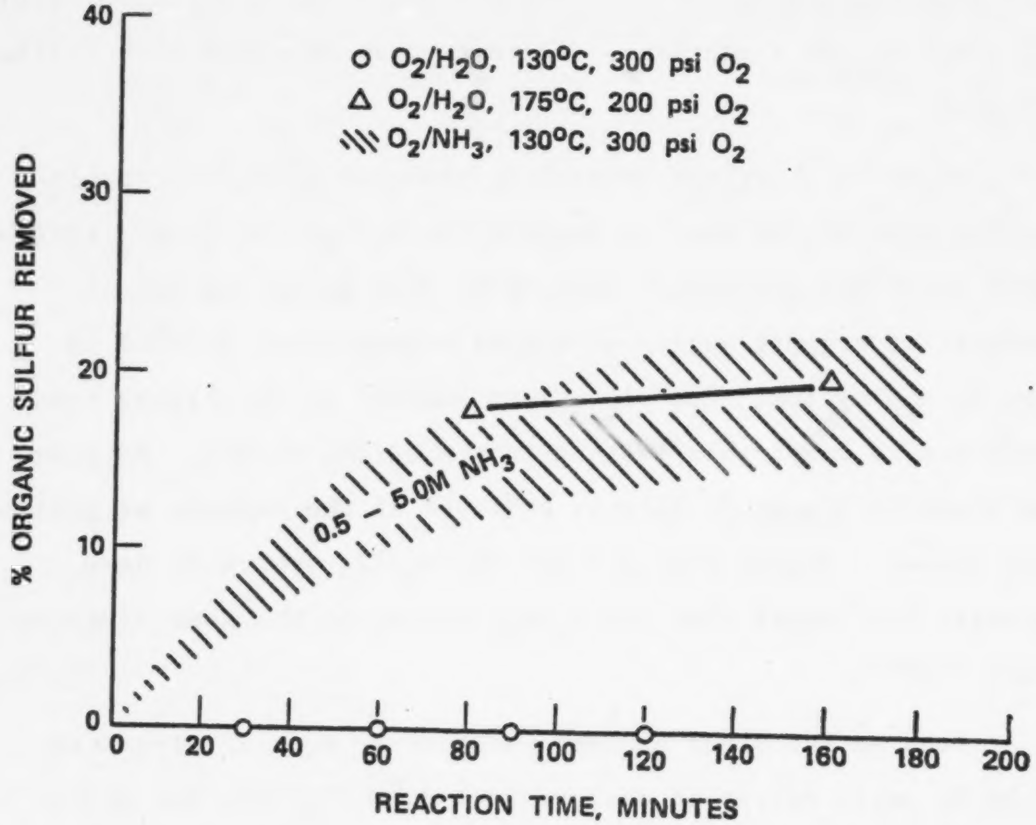

Figure 2. Organic Sulfur Removal for Various Oxydesulfurization Conditions

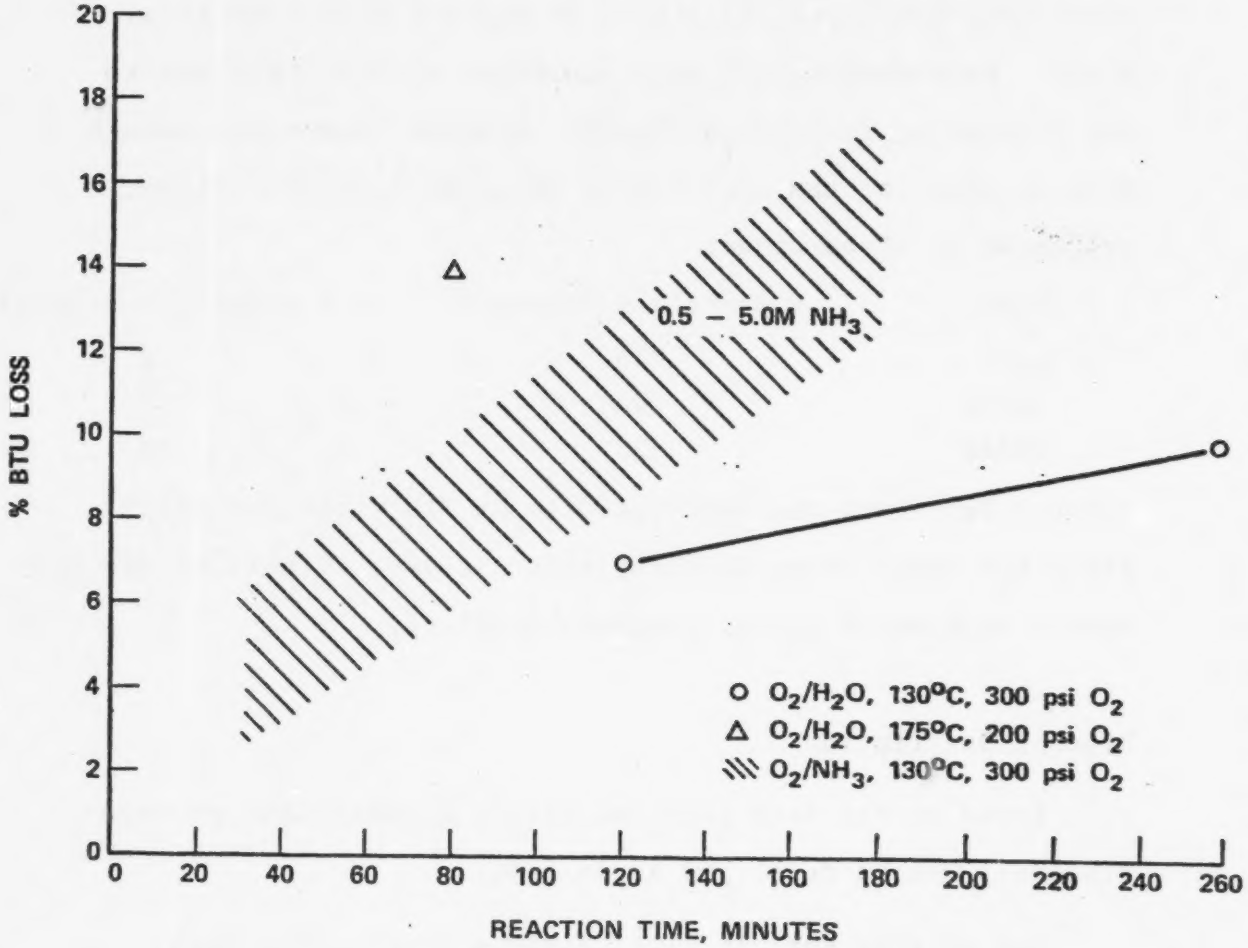

Figure 3. Btu Losses for Various Oxydesulfurization Conditions

organic sulfur removal and Btu yield should be anticipated with different coal types. Accordingly, the selection of the optimum leaching chemistry will depend on the amount of sulfur which must be removed from the coal, and on the organic sulfur removal and Btu losses for the specific coal.

We now need to project the performance that this process, when fully developed, is likely to achieve in a commercial plant. Performance will vary according to coal type and to the processing conditions chosen. However, there are enough data to pinpoint the most likely range of desulfurization, bracketed by three cases:

Case	% pyritic S removal	% organic S removal
90/0	90	0
90/20	90	20
95/40	95	40

Table 1 describes our best estimate of Btu yield and weight yield for these three leaching alternatives, as well as for the coarse wash which always precedes leaching.

Process Description

Based on the data just described, a commercial process flowsheet can be developed as follows.

Run of mine coal is first given a coarse coal wash.

Since chemical coal cleaning will generally produce a leached coal with a lower sulfur content than the standards that must be met, some of the washed coal will by-pass the

Slurry liquid	water	aq. NH_3	water
Temperature, °C	130	130	175-200
Sulfur removal,%			
pyritic	90	90	95
organic	0	20	40
Leach Btu yield,%	92	89	86
Leach weight yield,%	98	98	98
Wash Btu yield,%	90	90	90
Wash weight yield,%	85	85	85

Table 1. Assumptions for
various leaching conditions.

chemical cleaning plant as shown in Figure 4.

A simplified flowsheet of the chemical cleaning module of Figure 4 is shown in Figure 5. The process description has been reported earlier (Irminger and Petrovic, 1974; Agarwal et al., 1974; Sareen et al., 1975) but, for clarity, will be repeated here briefly, assuming the low-temperature O_2/H_2O process is used.

The portion of the coal to be chemically cleaned is crushed to -1/8" in an impact mill and then ball milled to -100 mesh in a water slurry.

The slurry is diluted to 20% solids and preheated to 130°C in Karbate heat exchangers and pumped into the reactors. For an 8,000 TPD plant, the reactors are acid brick lined pressure vessels, 33 in number, 9 ft diameter by 84 ft long, divided into 11 compartments furnished with agitators, and provide the coal with a residence time of 2 hrs. Vessels of this type and dimension are presently in use at hydrometallurgical plants in several countries.

An oxygen plant supplies oxygen at 300 psi pressure. The discharge slurry is cooled by passing it back through the heat exchangers. The clean coal is separated from the liquid phase in a thickener and a rotary filter, where it is washed clean. It is then balled on pelletizing disks and dried.

The overflow from the cleaned coal thickener is neutralized with lime or limestone. The resulting gypsum sludge is thickened, filtered, and discarded. The neutralized liquor is recycled for use as process water in the desulfurization reactors.

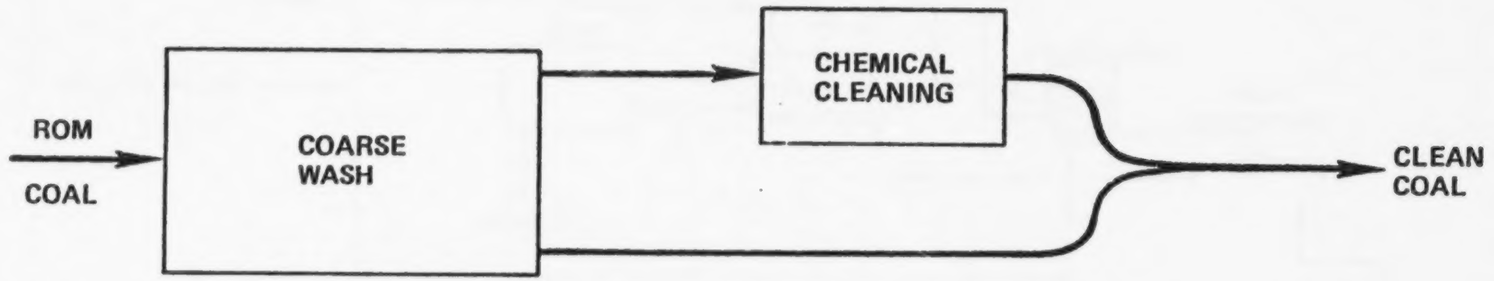

Figure 4. Overall Coal Cleaning Process

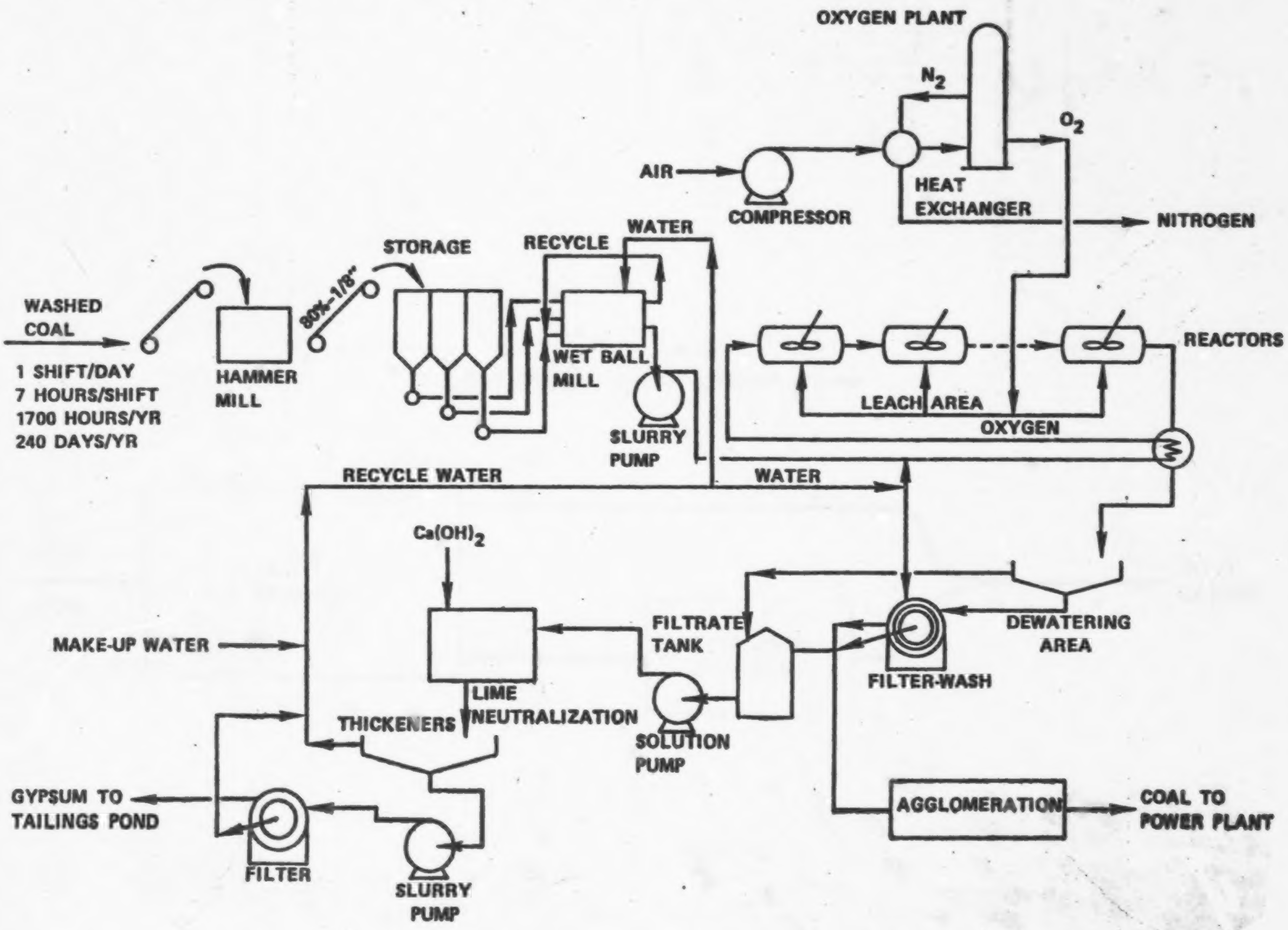

Figure 5. Flowsheet for O_2/H_2O Leaching of Pyritic Sulfur

Process Capital and Operating Costs

The capital and operating costs shown in Tables 2 and 3 are based on a commercial process as described. For some coals it may be desirable to perform the leaching at higher temperatures or in aqueous ammonia to enhance organic sulfur removal, as discussed; the costs for these process alternatives have not been calculated in detail, but are believed to be of the same order.

The capital cost for processing 8,000 TPD of coal totals $123 million in mid-1977 dollars, equivalent to $46.3/annual ton of coal feed. This estimate is based on a green-field plant, and includes all the required off-sites as well as contingency.

The operating cost, in Table 3, amounts to $23.5/ton clean coal, based on utility financing. Using this method of financing, an average annual capital charge of 15.9% results from depreciation, interest on debt, return on equity, taxes, and insurance.

This is the maximum cost of chemical coal cleaning, i.e. the cost when no portion of the coal can by-pass the chemical leaching section. Figure 6 shows the cost of clean coal as a function of the percent of the coarse-washed coal that can by-pass the chemical cleaning section so that the blend will still meet the desired standard. These costs range from $5.65/ton of product from coarse cleaning alone to $23.5/ton of product for chemical cleaning alone.

	Million $
Coal Handling and Washing	6.0
Crushing	8.4
Reactors	19.7
Oxygen Plant (1,000 TPD)	22.4
Liquid/Solid Separation	11.1
Neutralization	8.1
Agglomeration	14.3
Depreciable Investment	90.0
Land	1.0
Working Capital	14.4
Startup Costs	9.0
Interest during Construction	9.0
Total Investment	123.4

$/Annual Ton Leached = 46.3

Assumptions:

Mid 1977 dollars
Offsites and contingency factored into each process area
8,000 TPD coal feed to leaching

Table 2. Capital cost estimate for Kennecott Oxygen Leaching process.

	Million $/yr[1]
Process Losses[2]	9.7
Chemicals	
Lime	3.3
Flocculant	0.5
Binder	5.3
Utilities	
Steam	3.9
Electricity	7.9
Labor, Supervision	1.8
Direct Costs	32.4
Average Capital Charge[3] (15.9% total capital)	19.6
Maintenance, Labor & Supplies[4]	6.5
Plant Overhead (20% of labor & utilities)	2.7
Administrative Overhead (10% of labor)	0.2
Total Operating Cost	61.4
mill/KWH[5] = 9.54	
$/ton coal product = 23.5	

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1. Mid 1977 dollars; regulated utility financing
2. 17.2% overall Btu loss, including 10% Btu loss in conventional coal cleaning. Cost figured at $18/ton ROM coal.
3. Includes depreciation, interest on debt, return on equity, insurance, and taxes
4. 9% of depreciable capital, excluding contingency
5. 8,000 TPD plant produces 2.61 MM TPY product containing 12,000 BTU/lb

Table 3. Operating cost estimate for Kennecott Oxygen Leaching process.

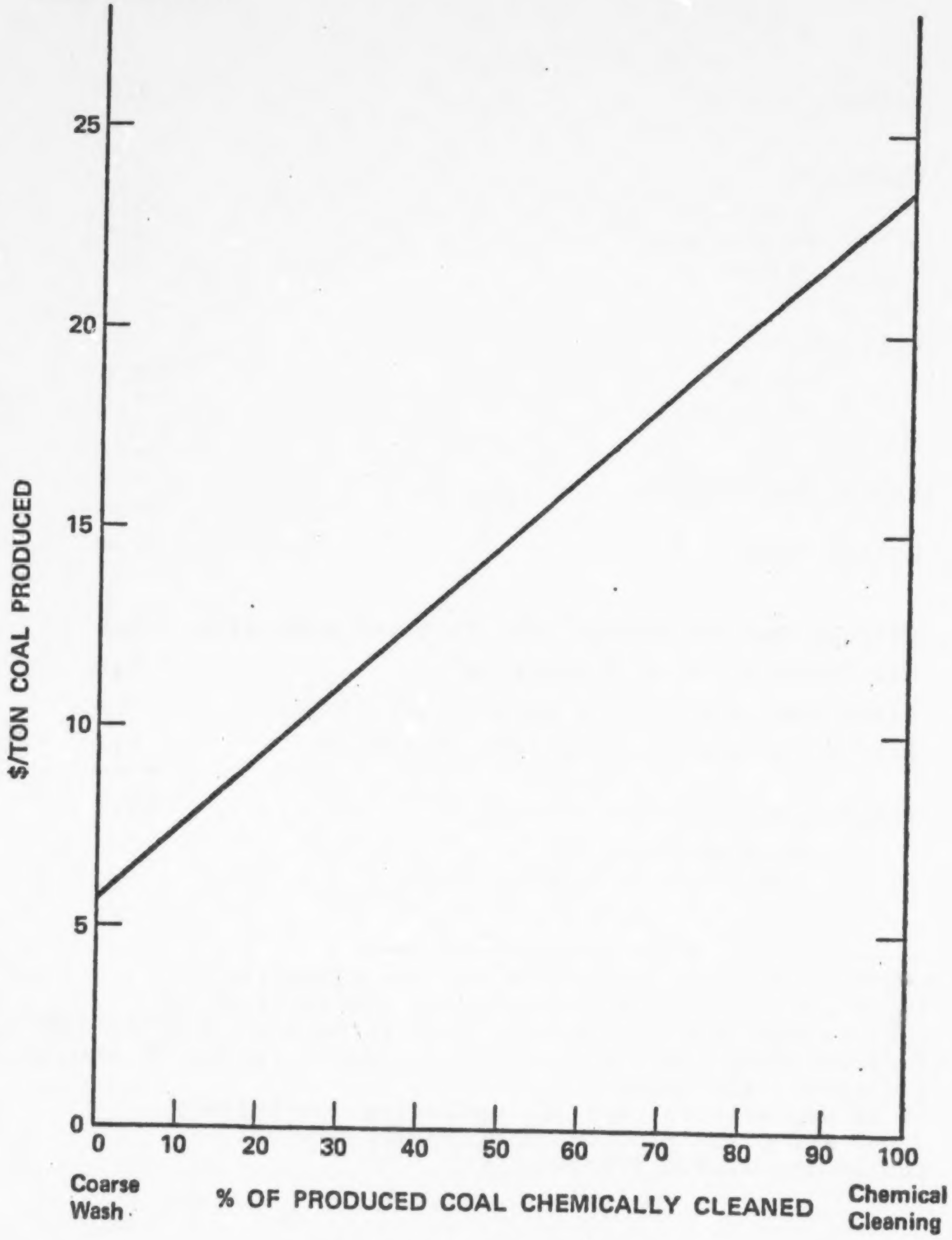

Figure 6. Cost of Coal Cleaning

Definition of Compliance Coal

For the purpose of this study it is necessary to define the standard to which the coal must be desulfurized in order to be considered a suitable product of chemical cleaning.

There is considerable controversy at this time with regard to New Source Performance Standards for fossil-fired power plants. The selection of standards for this analysis is difficult and subject to possible criticism. Nevertheless, two levels of emissions were chosen and the technique can be applied for any standards that are ultimately promulgated. The selected levels are 1.2#SO_2/MMBtu, the present New Source Performance Standard and a level required of some existing plants, and 2.7#SO_2/MMBtu, a more liberal standard for existing plants.

Estimate of Production and Reserves of Coal Available to Chemical Coal Cleaning

Based on coal seam data on pyritic sulfur content, organic sulfur content, and calorific value, reported by Cavallaro, Johnston, and Deurbrouck (1976) and by Wizzard (1978), projections have been made of the production and reserves which can meet our postulated standards of 1.2, respectively 2.7, lb SO_2 per million Btu by chemical coal cleaning, but not by coal washing alone. All three process variants, 90/0, 90/20, and 95/40, were used in these projections.

Table 4 shows the results in terms of the annual tonnage of low-sulfur coal thus produced. It shows that a 10-28%

Region	1975 Production (MM net ton)	Incremental Clean Coal Production, MM net t/yr					Cleaning Cost ($/t)
		Raw	Washed	Chemically Desulfurized			
				90/0	90/20	95/40	
a) Clean coal specification: 1.2 lb SO_2/MM Btu							
Northern Appalachian	182	7	12	26	37	70	17-20
Southern Appalachian	192	67	25	29	54	77	10
Alabama	23	7	0	7	10	12	20
Eastern Midwest	142	1	1	4	7	19	19-22
Western Midwest	10	0	5	1	1	2	16-20
Western	85	60	11	0	0	0	---
"Other"	15	--	--	--	--	--	---
TOTAL	650	140	54	67	109	180	
% of U.S. Production	100	22	8	10	17	28	
b) Clean coal specification: 2.7 lb SO_2/MM Btu							
Northern Appalachian	182	46	36	59	68	74	16-17
Southern Appalachian	192	173	16	0	0	0	---
Alabama	23	17	1	4	4	4	11-12
Eastern Midwest	142	4	8	43	62	91	17-18
Western Midwest	10	1	1	2	3	5	18-20
Western	85	80	-4	-0	-0	0	---
"Other"	15	--	--	--	--	--	---
TOTAL	650	321	66	108	137	174	
% of U.S. Production	100	49	10	17	21	27	

Table 4. Incremental clean coal production: Raw, washed and chemically desulfurized.

increase in U.S. coal production meeting a 1.2#SO_2/MMBtu standard can potentially be achieved by chemically cleaning coal. The bulk of this production is from Appalachian coals. For the 2.7#SO_2/MMBtu standard a 17-27% increase is projected with most of the increase coming from Northern Appalachia and Eastern Midwest.

Note that the cleaning costs in Table 4 are competitive with recently announced purchase prices for low-sulfur coal.

Table 5 shows the results in terms of potential reserves of low-sulfur coals created by the advent of chemical cleaning. (To make this projection it was necessary to assume that the coal seam data not only characterize U.S. production, but also U.S. reserves.)

To illustrate with an example how these data were derived, Figure 7 shows the case for coal from the Southern Appalachian region complying with a standard of 1.2#SO_2/MMBtu. The distribution curves for raw coal and washed coal are taken from the cited literature. Because these data indicate that up to 50% of all coal from this region complies with the standard if washed, only that portion of each curve is shown which refers to the non-complying coal. The distribution curves for leached coal are calculated from the raw coal data according to the procedure described below, and are shown for the three process alternatives: 90/0, 90/20, and 95/40.

It can be shown from Figure 7 that if, say, the 90/0 alternative is used, this will make available an additional 18%

Region	Reserves (billion t)	Incremental Clean Coal Reserves, Billions Tons				
		Raw	Washed	Chemically Desulfurized		
				90/0	90/20	95/40
	a) Clean coal specification:			1.2 lb SO_2/MM Btu		
Northern Appalachian	68	3	5	10	14	26
Southern Appalachian	35	12	5	5	10	14
Alabama	2	1	0	1	1	1
Eastern Midwest	89	1	1	2	4	12
Western Midwest	16	0	8	2	2	3
Western	22	15	5	0	0	0
TOTAL	230	32	24	20	31	56
% of U.S. Reserves	100	14	10	9	13	24
	b) Clean coal specification:			2.7 lb SO_2/MM Btu		
Northern Appalachian	68	17	13	22	25	28
Southern Appalachian	35	32	3	0	0	0
Alabama	2	1	0	0	0	0
Eastern Midwest	89	3	5	27	39	57
Western Midwest	16	1	1	3	5	8
Western	22	21	1	0	0	0
TOTAL	230	75	23	52	69	93
% of U.S. Reserves	100	33	10	23	30	40

*Assumes sulfur distribution in reserves is the same as in 1975 production

Table 5. Incremental clean coal reserves:
Raw, washed, and chemically desulfurized.*

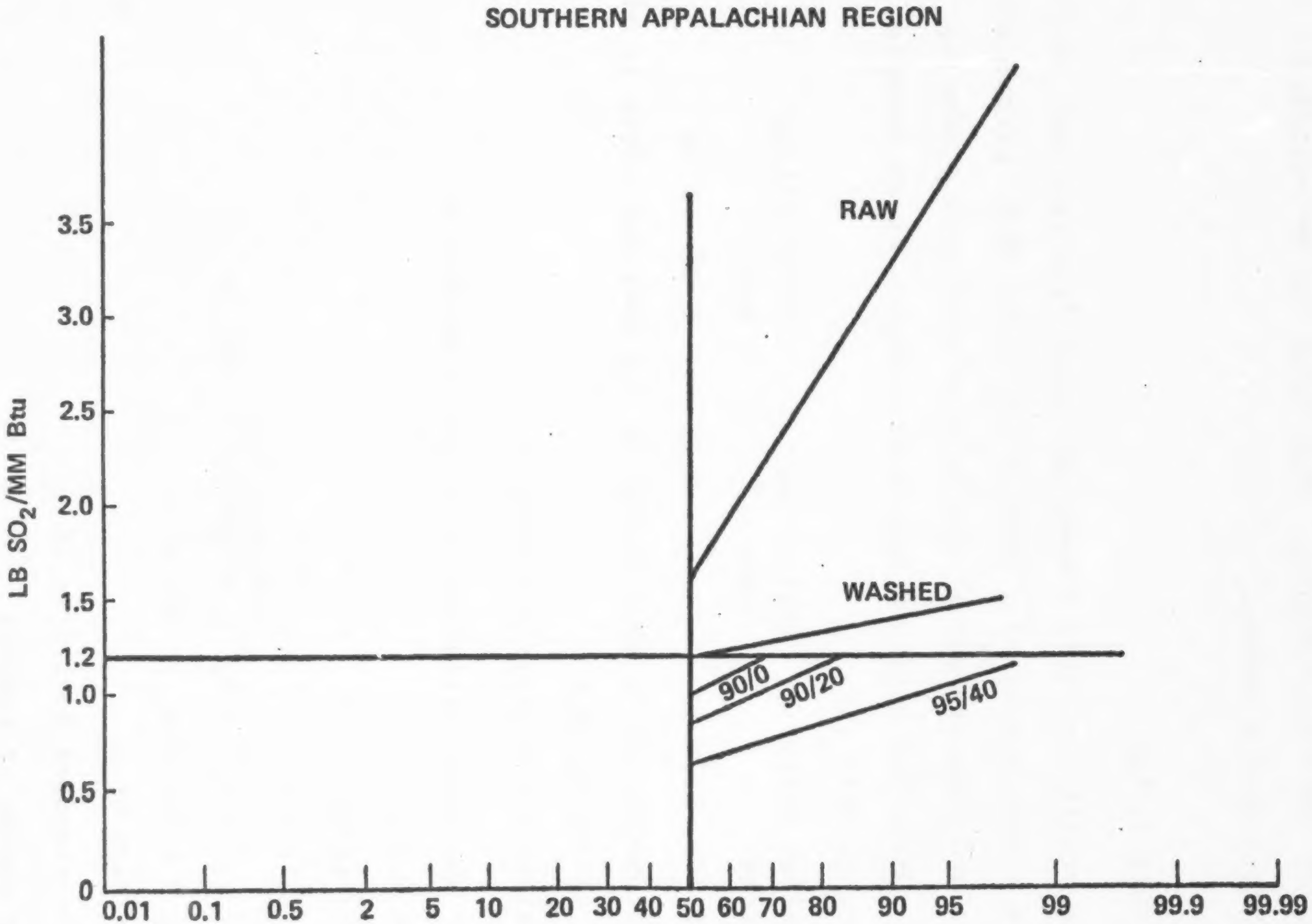

Figure 7. Coals in Southern Appalachian Region Capable of Meeting 1.2# SO/MM Btu Standard after Various Treatments

of all Southern Appalachian coal.

It also shows that the compliance blend of washed coal and 90/0 leached coal averages 75% washed coal and 25% leached coal for the entire region. This value can be verified by integrating both curves.

Sample Calculation

The results in Table 4 were generated from raw coal sulfur analyses (Cavallaro et al., 1976 and Wizzard, 1978) presented as means and standard deviations (σ) for each coal-producing region. Using the Southern Appalachian region as an example, the raw coal data are:

Pyritic Sulfur		Organic Sulfur		Total Sulfur	
Mean	σ	Mean	σ	Mean	σ
0.46	0.72	0.62	0.22	1.08	0.88

The small amount of sulfate sulfur in the coal was added to the pyritic sulfur so that

Pyritic S + Organic S = Total S

For any three variables x, y, and z related by

$x + y = z$

it can be shown that:

1) $\bar{x} + \bar{y} = \bar{z}$

2) $\sigma_z^2 = \sigma_x^2 + \sigma_y^2 + \frac{2\Sigma(x_i y_i)}{N} - 2(\bar{x})(\bar{y})$

where x_i = individual values of x

$\bar{x}$ = mean of x_i

σ_x = standard deviation of x_i

N = number of samples

Furthermore, if a variable w is defined by

$$w_i = kx_i$$

where

k is a constant,

then

$$\bar{w} = k\bar{x}$$

$$\sigma_w = k\sigma_x$$

Using the above relations, and assuming given percentages of pyritic and organic sulfur removal, one can find the mean and the standard deviation of total sulfur in desulfurized coal. For pyritic/organic removals of 90/0, 90/20, and 95/40, the Southern Appalachian region can be calculated to yield:

	90/0		90/20		95/40	
	Mean	σ	Mean	σ	Mean	σ
Total Sulfur in Cleaned Coal	0.666	0.273	0.542	0.230	0.395	0.158

The calorific value of the chemically cleaned coal is estimated using the weight yields and Btu yields shown in Table 1. Again, for Southern Appalachian coal, these produce calorific values of:

	Raw Coal	90/0	90/20	95/40
Btu/lb	13,314	13,234	12,803	12,371

Therefore, the SO_2 emissions from Southern Appalachian coal will be:

	90/0		90/20		95/40	
	Mean	σ	Mean	σ	Mean	σ
lb SO_2/MMBtu	1.006	0.412	0.846	0.359	0.638	0.255

These three distributions are plotted in Figure 7 and indicate the following incremental amount of raw coal available to chemical leaching, over and above the 50% that would comply by washing only:

	90/0	90/20	95/40
% of Non-Washable Coals Meeting Standard	18	34	49

The average blend of washed and leached coal, obtained by integration of the distribution curves over the region, is:

	90/0	90/20	95/40
Clean Coal Blend (washed:leached)	75:25	73:27	76:24

These blend projections are conservative. Lower overall costs could be achieved by using more washed-only coal for blending, but this would lower the tonnage of coal available from the region.

For 1975, total production from the Southern Appalachian region was 192 million tons (Keystone, 1977). Assuming this tonnage to be typical, and assuming a 90/0 sulfur removal, raw coal suitable as feed to chemical coal cleaning plants is (192)(0.18) = 35 million tons per year in this region. The clean coal thus produced will be somewhat less, due to losses in washing and leaching, and is calculated as follows:

$$(192)(0.18)\left[(0.75)(0.85)+(0.25)(0.83)(0.92)\right] = 29 \text{ million TPY}$$

Explanation:

0.75 = fraction of blend which is coarse-washed only

0.85 = weight yield after coarse wash (Table 1)

0.25 = fraction of blend which is washed and leached

0.83 = weight yield after washing (85% yield) and leaching (98% yield)

0.92 = adjustment for 8% parasitic consumption of clean coal for power and steam consumed in leach plant.

The cleaning cost of $10/ton, shown in Table 4, was derived from Figure 6 for a 75:25 blend.

Chemical Coal Cleaning vs. Stack Gas Scrubbing: Performance Comparison

As shown in the preceding projections, large tonnages of high-sulfur coal can be made to conform to stringent sulfur emission standards by chemical cleaning. These results can generally also be achieved by stack gas scrubbing, and the final decision must therefore be based on economics, which will be discussed in the next section.

On the other hand, scrubbing is reported as able to remove in excess of 85% of the sulfur dioxide in the flue gas. Chemical coal cleaning, on the other hand, removes varying fractions of sulfur, depending on the coal and on the leaching variant, but seldom removes much more than 70% of the sulfur. This would pose a problem in new plants requiring 85% sulfur removal.

Chemical Coal Cleaning vs. Stack Gas Scrubbing: Economic Comparison

Sulfur dioxide scrubbers must be sized for the full power plant generating capacity. Because the fixed charges must be distributed over the actual kWh generated, the cost of scrubbing in mills per kWh is high for plants with low load factors. Coal cleaning, on the other hand, is decoupled from boiler operation, and the cost of coal cleaning in mills per kWh is independent of load factor.

Figure 8 shows a cost comparison between chemical coal cleaning and stack gas scrubbing. The coal cleaning costs are the figures derived in the preceding calculations. The scrubbing costs are escalated from a Tennessee Valley Authority report (McGlamery et al., 1975), and are based on wet lime and wet limestone scrubbing because they account for 70% of currently installed or planned scrubbing capacity. Both scrubbing costs and coal cleaning costs are expressed in mid-1977 dollars and assume regulated utility financing, i.e., 15.9% of capital cost charged to annual operating cost. Neither cost includes particulates collection.

Chemical coal cleaning costs, as well as scrubbing costs, contain site-specific cost components which cannot be reflected with precision in a generalized comparison such as Figure 8. Coal cleaning costs depend significantly on local environmental standards and on the quality of the coal. Scrubbing costs vary greatly with site-specific factors, as reflected in the high variance of actual plant cost experience. Nevertheless, Figure 8 shows that within the most common load factor range, coal cleaning costs should clearly be comparable to scrubbing costs.

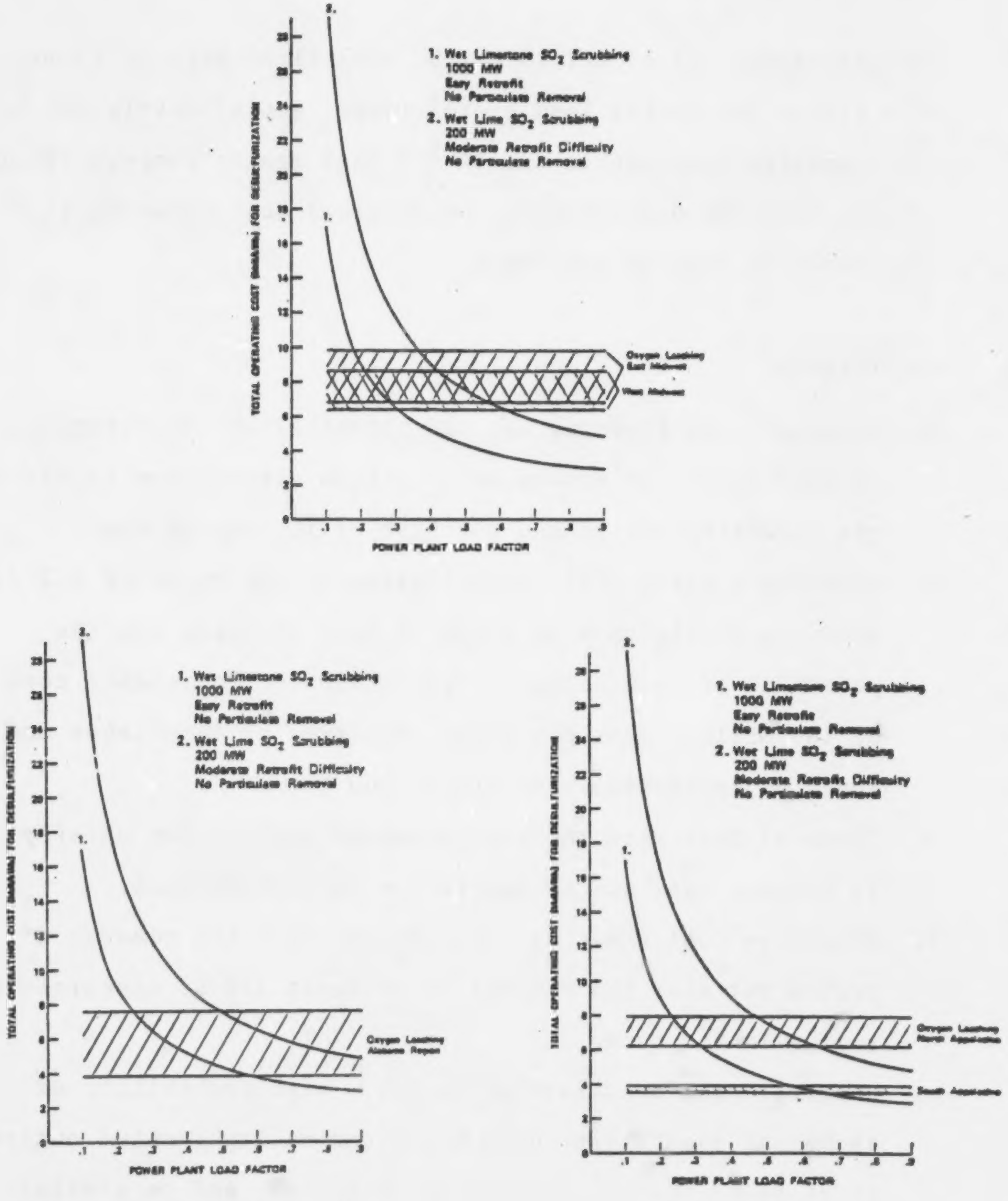

Figure 8. Comparative Economics of SO_2 Scrubbing vs. Chemical Cleaning
– 1977 Dollars –

(Approximately 74% of all 1976 U.S. coal-fired utility capacity fell within the 35-65% load factor range; approximately 56% of U.S. capacity fell within the 40-60% load factor range.) Figure 9 shows that the capital costs of chemical coal cleaning is comparable to that of scrubbers.

Conclusions

1. Chemical coal cleaning has the potential of constituting, in many cases, an economically viable alternative to stack gas scrubbing and to the purchase of low-sulfur coal.
2. Assuming a clean coal specification in the range of 1.2-2.7 lb SO_2 per million Btu, chemical coal cleaning has the potential of increasing the production of compliance coal by 180 million tons per year. Reserves of compliance coal would be increased by 60-90 billion tons.
3. Chemical coal cleaning has potential application chiefly in Eastern coal states and in the Eastern Midwest.
4. Effective coal cleaning requires not only the removal of pyrite but also the removal of at least 20% of the organic sulfur in the coal.
5. Chemical coal desulfurization has a high probability of technical feasibility because it can be implemented entirely in state-of-the-art industrial equipment, and is similar in many respects to existing hydrometallurgical process plants.

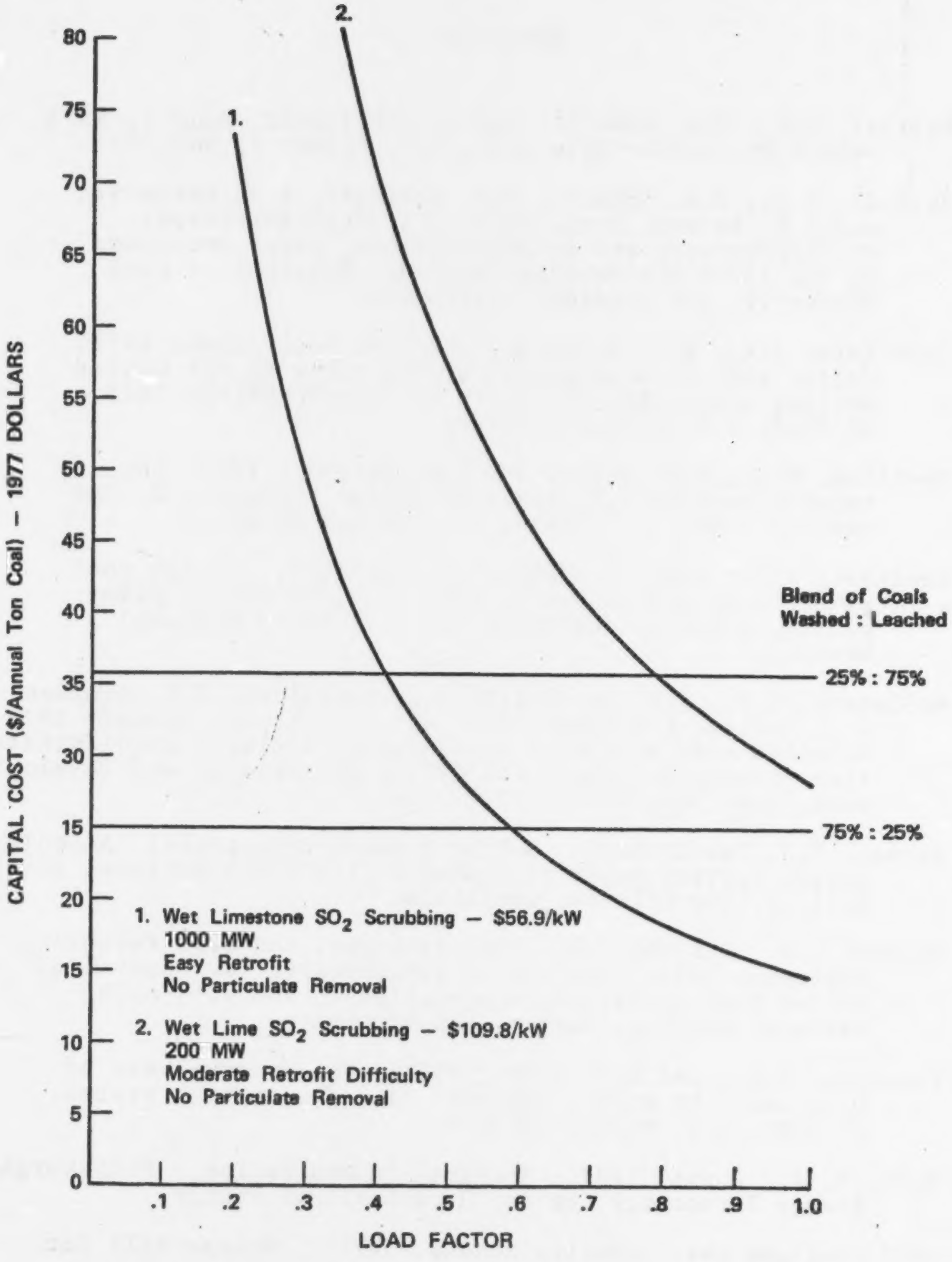

Figure 9. Capital Cost of SO_2 Scrubbing and Chemical Coal Cleaning

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to convert from	to (SI units)	multiply by
Btu	joule	1,055.87
kWh	joule	3.60×10^6
pounds	kilogram	0.4536
tons (short)	kilogram	907.18
tons (metric)	kilogram	1,000.00
minutes	seconds	60.00
hours	seconds	3,600.00
days	seconds	86,400.00

Table 6: Conversion factors.

JPL COAL DESULFURIZATION PROCESS BY LOW TEMPERATURE CHLORINOLYSIS

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California Institute of Technology
Pasadena, California

ABSTRACT

The Jet Propulsion Laboratory of the California Institute of Technology has conducted an extensive laboratory scale investigation under a U.S. Bureau of Mines contract of 12 coals including bituminous, sub-bituminous and lignite coals for desulfurization by a three-stage process that includes chlorination, hydrolysis and dechlorination. Results are represented for organic, pyritic, and total sulfur removal. A parametric study of operating conditions was conducted. A unique feature of the process is that high organic sulfur removal is demonstrated in conjunction with high-pyritic sulfur removal for total sulfur removal under favorable operating conditions of greater than 70 percent. Preliminary costing of the desulfurization process indicates competitive costs relative to other coal desulfurization processes and flue gas desulfurization. Further development work on the process is continuing under U.S. Department of Energy auspices. The future development activity includes a bench-scale continuous flow mini-pilot plant operation at 2 kilograms coal feed per hour and a bench-scale batch operation at 2 kilograms of coal per batch. A preliminary equipment design is presented for the continuous flow mini-plant coal desulfurization operation.

INTRODUCTION

The Jet Propulsion Laboratory (JPL) of the California Institute of Technology has investigated the use of chlorination for the oxidation of both pyritic and organic sulfur contained in bituminous coals for accomplishing coal desulfurization to meet Environmental Protection Agency stack emission standards of 1.2 pounds SO_2 per million thermal B.t.u.'s. For coals with a heating value of 12,000 B.t.u. per pound acceptance standards translate to 0.7 weight percent sulfur in the coal.

The early research activity was carried out by JPL under internal funding to devise the basic elements of the process. Preliminary findings indicated that coal desulfurization on Illinois No. 6 bituminous coal having a total sulfur content of 4.77% sulfur with approximately equal distribution of organic and pyritic sulfur demonstrated approximately 70% organic sulfur reduction, up to 90% pyritic sulfur reduction and 76% total sulfur reduction (Hsu, et al., 1977). The laboratory scale research reported here and under sponsorship of the U.S. Bureau of Mines represents additional data obtained on 12 high sulfur coals including 9 bituminous, 2 sub-bituminous, and 1 lignite coals, Table 1. The coals have been treated under the conditions of chlorination, hydrolysis and dechlorination constituting the JPL coal desulfurization process. The research work is continuing under the U.S. Department of Energy sponsorship. The follow-on activity will include bench-scale, batch tests at 2 kg of coal per batch and construction and operation of an integrated continuous flow, mini-pilot plant to demonstrate the process at a coal feed rate of 2 kg/hr.

ERDA PSOC Number	Seam, County & State	Rank	Ash Content (Wt.%)	Sulphur Content, Wt. %		
				Organic	Pyritic	Total
108	Pittsburgh, Washington, Pennsylvania	HVA (Bit.)	9.50	1.07	2.06	3.13
219	Kentucky #4, Hopkins, Kentucky	HVA (Bit.)	8.06	1.08	1.40	2.56
190	Illinois, #6, Knox, Illinois	HVA (Bit.)	8.49	1.90	1.05	3.05
276	Ohio #8, Harrison, Ohio	HVA (Bit.)	11.19	2.24	2.07	5.15
026	Illinois #6, Saline, Illinois	HVC (Bit.)	10.84	2.08	4.23	6.66
342	Clarion, Jefferson, Pennsylvania	HVA (Bit.)	9.19	1.39	5.01	6.55
240A1	Big D, Lewis, Washington	Sub-bit B	29.40	1.75	1.60	3.36
097	Seam 80, Carbon, Wyoming	Sub-bit A	9.80	0.84	0.38	1.23
086	Zap, Mercer, N. Dakota	Lignite	11.49	0.63	0.56	1.22
213	Kentucky #9	HVB (Bit.)	9.36	1.86	1.89	3.32
PHS-398 (BOM)*	Raw Head, 3A, Upper Freeport Seam, Somerset, Pennsylvania	-	19.7	0.46	2.26	3.01
PHS-513 (BOM)*	Mine 513, Upper Clarion, Butler, Pennsylvania	-	-	1.76 (Physically cleaned, high organic coal)	<0.2	1.76

---

* Samples received from Dr. Scott R. Taylor, Department of Energy, Pittsburgh, Pennsylvania.

Table 1. Selected Coals for Chlorinolysis Experiments Under Bureau of Mines-Sponsored Program

LABORATORY SCALE PROCESS STUDIES

The laboratory coal processing for coal desulfurization by the JPL low temperature chlorinolysis process is depicted in Figure 1.

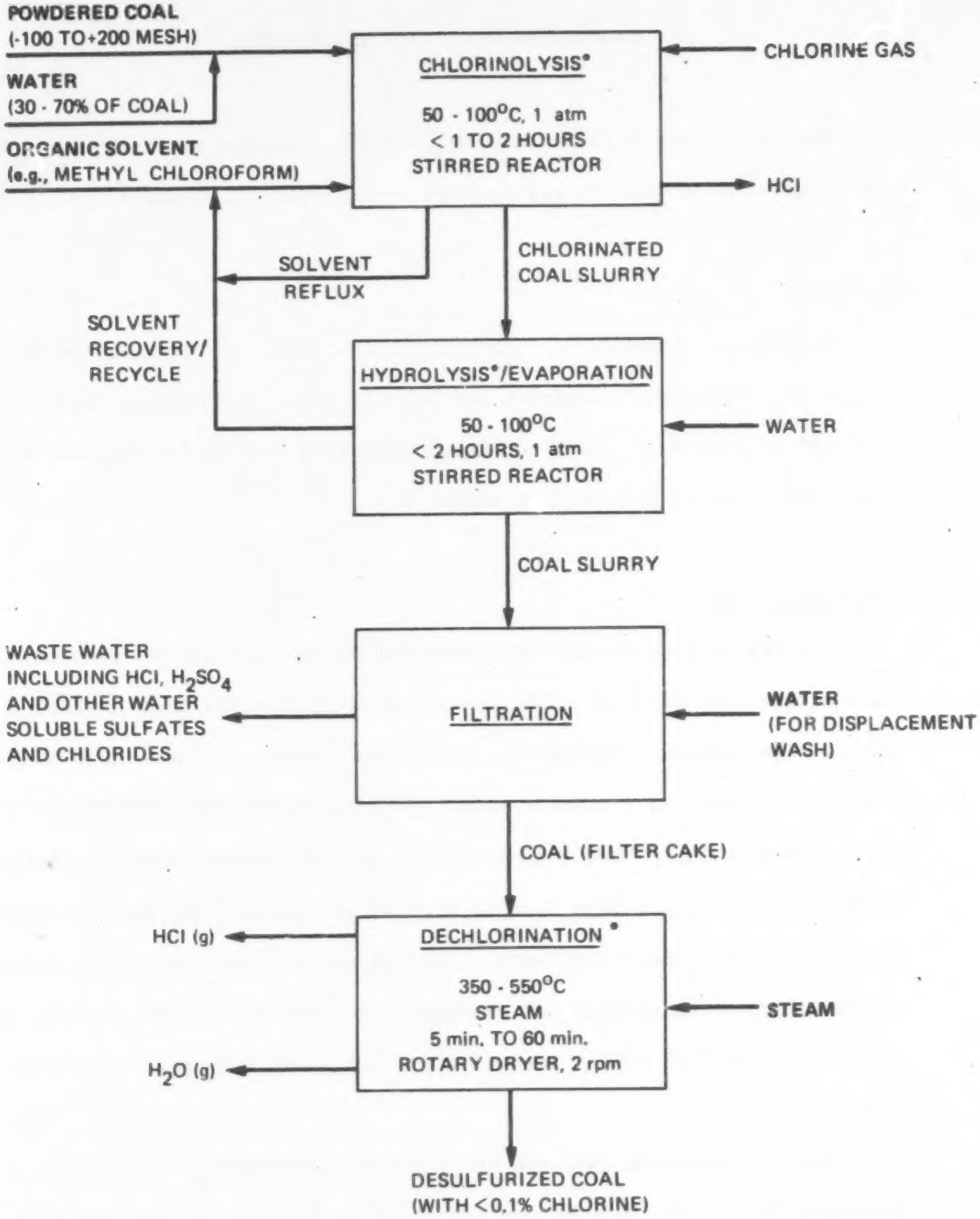
Apparatus

Laboratory apparatus for chlorination of the coal is depicted in Figure 2. Laboratory apparatus for hydrolysis of chlorinated coal is depicted in Figure 3. Dechlorination apparatus for the chlorinated and hydrolyzed coal is depicted in Figure 4.

Laboratory Data

Laboratory data on the coal desulfurization process is summarized in Table 2 for coal PSOC-219 (HVA Bit, Ky #4, Hopkins, Ky) and in Table 3 for 11 other eastern, midwestern and western coals. A total of 9 bituminous, 2 sub-bituminous and 1 lignite coals has been tested that represents a total sulfur content in the raw coal from 1.22 to 6.66 weight percent. Organic sulfur content ranges from 0.46 to 2.24 weight percent and pyritic sulfur from <0.2 to 5.01 weight percent. Sulfate sulfur constitutes the remaining sulfur in the coal samples and averaged less than 0.2 weight percent for 9 coals, 0.29 to 0.35 weight percent for 2 coals and 0.84 weight percent for 1 coal.

Coal samples were analyzed by Galbraith Laboratories, Knoxville, Tennessee for sulfur composition and chlorine in both the raw and treated coal samples. Ultimate analyses were conducted on several treated coal samples. Water wash, water scrubber solutions and gas samples were also analyzed for given tests to obtain material balances.



*LABORATORY GLASSWARE EQUIPMENT FOR THESE PROCESSES IS SHOWN IN FIGURES 2, 3 AND 4.

Figure 1. Process flow diagram for laboratory scale coal desulfurization

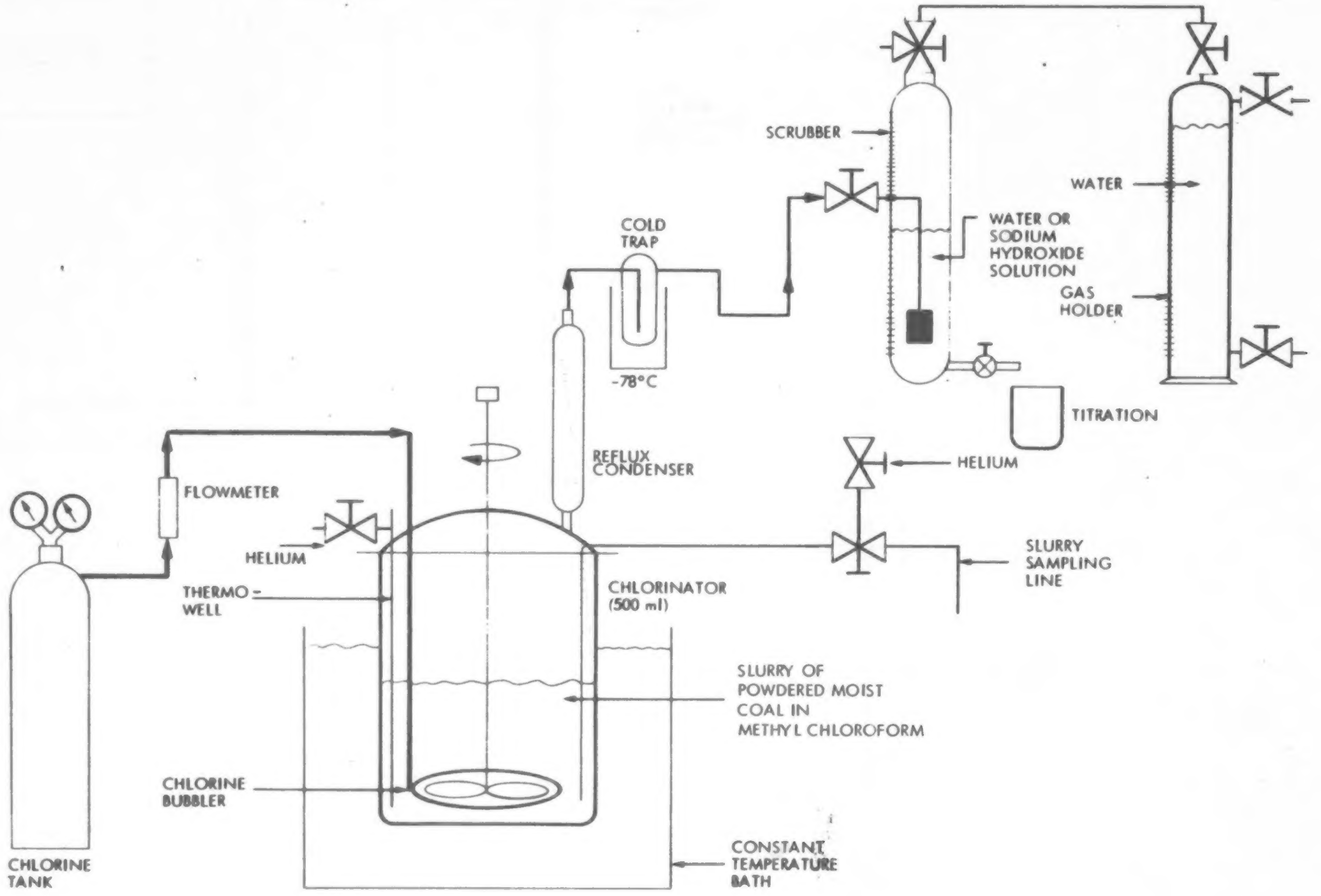


Figure 2. Laboratory glassware apparatus for chlorination of coal

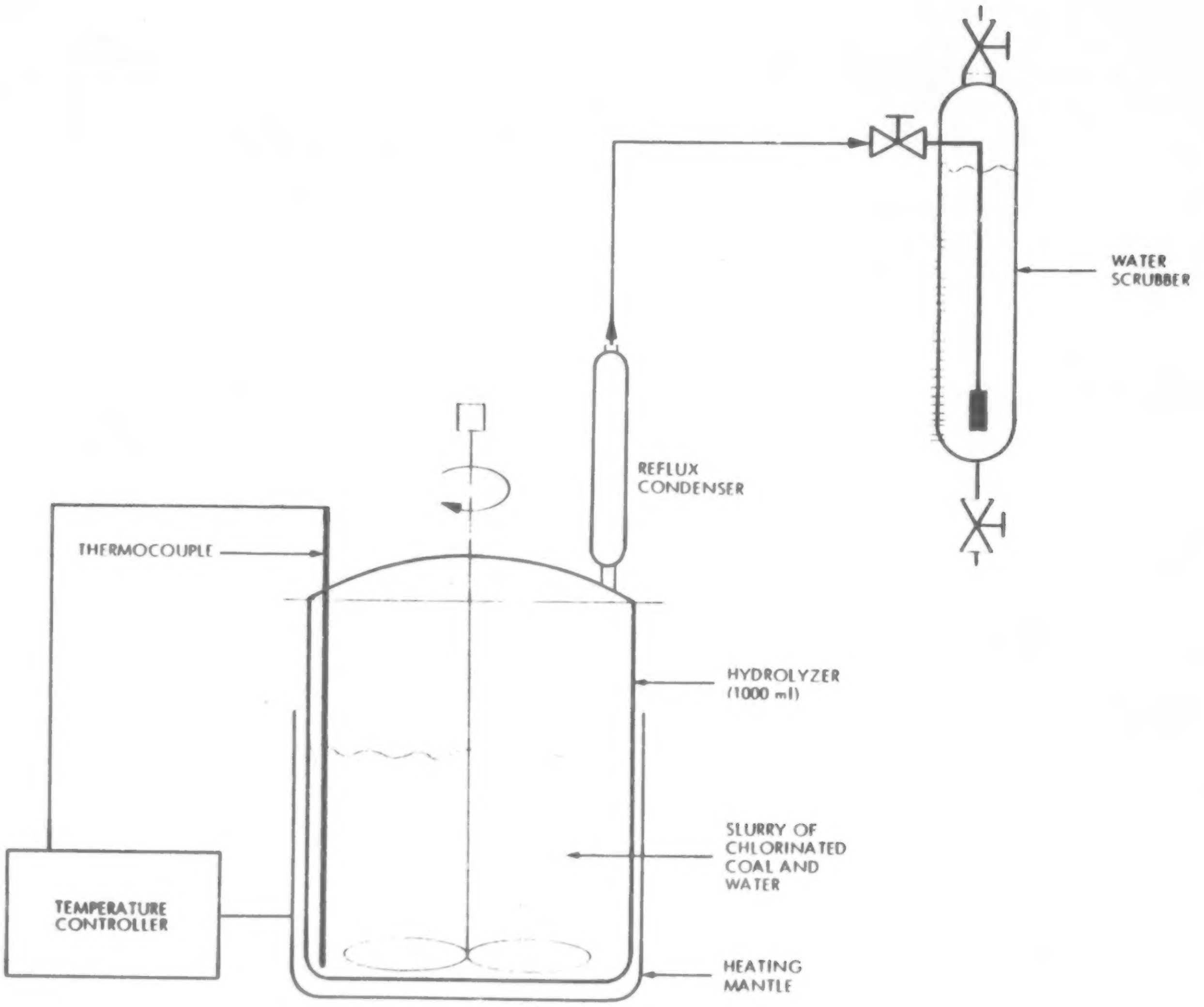


FIGURE 3. LABORATORY GLASSWARE APPARATUS FOR HYDROLYSIS OF CHLORINATED COAL

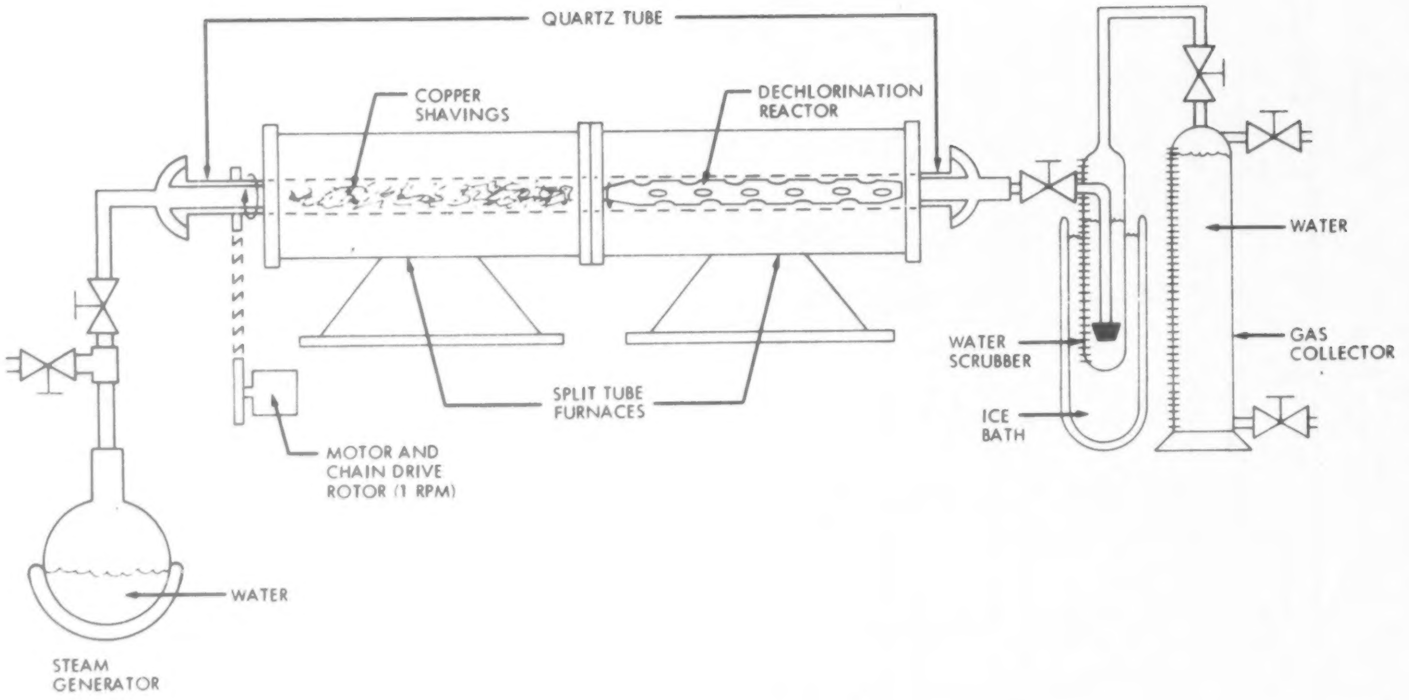


Figure 4. Laboratory equipment for dechlorination of coal

CHLORINATION: 500 ml stirred flask; 100 gram sample of -100 to +200 mesh coal; atm. pressure; 74°C; $Cl_2(g)$ at 0.75 g/min; methyl chloroform/coal at 2; water/coal at 0.5.

HYDROLYSIS: 1000 ml stirred flash; 60-100°C; water/coal at 2-4 per wash; 5-60 minutes per wash; filtration water wash/coal at 1-2; 1 to 2 washes.

DECHLORINATION: 1-inch diameter quartz rotary tube at 1-2 RPM in split tube furnace; coal at 2 to 4 grams/batch; steam atm. at 0.4 to 110 grams/hour; temp. of 350 to 550°C; 15 to 75 minutes.

Ave No. of Runs	Chlorination Time (Min.)	Residual Sulfur Analysis (Wt. %)				Sulfur Removal (%)			Dechlorination Residual Cl (wt. %)	
		Organic	Pyritic	Sulfate	Total	Organic	Pyritic	Total	Before	After
		COAL PSOC-219, HVA BIT. KY. NO. 4, HOPKINS, KY.								
RAW COAL		1.08	1.40	0.08	2.56					
1	10	0.78	0.79	0.04	1.61	28	44	37	4.8	
1	20	0.69	0.73	0.11	1.50	36	48	41	4.9	0.12
6	30	0.82	0.41	0.07	1.39	27	71	46	5.4	0.37
9	60	0.59	0.31	0.05	0.95	45	78	63	10.4	0.42
2	120	0.45	0.48	0.14	1.07	58	65	58	14.6	0.36
WATER/COAL - 0.3										
2	30	0.57	0.75	0.04	1.37	47	46	46	4.74	0.95
2	60	0.56	0.40	0.06	1.00	48	71	61	8.86	0.21
2	120	0.70	0.28	0.06	1.04	45	79	59	18.9	0.26
WATER/COAL - 0.7										
2	30	0.78	0.45	0.01	1.24	28	68	51	5.1	0.17
2	60	0.63	0.47	0.02	1.15	41	66	55	9.2	0.53
2	120	0.71	0.41	0.03	1.14	34	71	55	11.4	1.16
TEMP. - 50°C										
2	30	0.78	0.35	0.02	1.15	28	75	55	-	0.45
2	60	0.69	0.13	0.01	0.83	36	91	67	-	0.52
2	120	0.54	0.25	0.05	0.84	50	82	67	18.6	0.50
TEMP. -60°C										
1	30	0.71	0.16	0.01	0.87	34	89	66	-	-
1	60	0.72	0.18	0.07	0.96	40	87	62	8.6	0.47
1	120	0.74	0.08	0.03	0.74	46	94	71	22.3	0.50
TEMP. - 85°C										
1	60	0.65	0.35	0.12	1.12	40	75	56	11.3	0.86
$Cl_2(g)$ - 0.375 g/min										
1	120	0.30	0.63	0.38	1.31	72	55	49	11.3	0.31
$Cl_2(g)$ - 1.50 g/min										
2	30	0.48	0.56	0.25	1.30	56	60	49	6.3	0.57
1	60	0.33	0.19	0.40	0.96	69	86	62	13.1	1.00
1	120	0.70	0.04	0.18	0.92	35	97	64	19.8	-
SOLVENT - CARBON TETRACHLORIDE										
1	30	0.72	0.31	0.01	1.03	33	78	60	-	0.21
2	60	0.74	0.43	0.08	1.20	37	69	53	8.8	0.15
2	120	0.64	0.50	0.05	1.19	40	64	53	9.0	0.96
SOLVENT - TETRACHLOROETHYLENE AT 74°C										
1	15	0.99	0.34	0.02	1.35	8	76	47	-	1.29
1	20	0.77	0.30	0.13	1.20	29	79	53	24.4	1.14
2	30	0.66	0.57	0.07	1.30	39	59	49	11.2	0.41
3	60	0.55	0.53	0.05	1.13	49	62	56	15.3	1.01
1	120	0.66	0.46	0.05	1.18	37	67	54	17.1	0.64
SOLVENT - TETRACHLOROETHYLENE AT 100°C										
1	15	0.66	0.77	0.01	1.44	39	45	44	-	0.44
1	30	1.00	0.14	0.01	1.14	7	90	56	-	0.31
1	60	0.73	0.42	0.05	1.21	32	70	53	23.1	0.39

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TABLE 2
Laboratory Coal Desulfurization Data
Chlorination Reaction Parameters, Coal PSOC-219

CHLORINATION:	500 ml stirred flask; 100 gram sample of -100 to +200 mesh coal; atm. pressure; 74°C; $Cl_2(g)$ at 0.75 g/min; methyl chloroform/coal at 2; water/coal at 0.5.
HYDROLYSIS:	1000 ml stirred flask; 60-80°C; water/coal at 4/wash; 60 min./wash; filtration water wash/coal at 1; 1-2 washes.
DECHLORINATION:	1-inch diameter quartz rotary tube at 1-2 RPM; 2-4 grams coal; steam atm. at 0.4 - 110 grams/hour; 400-500°C; 30-60 minutes.

Ave. No. of Runs	Chlorination Time (Min.)	Residual Sulfur Analysis (Wt. %)				Sulfur Removal (%)			Dechlorination Residual Cl (Wt. %)	
		Organic	Pyritic	Sulfate	Total	Organic	Pyritic	Total	Before	After
EASTERN COALS										
PHS-513, BITUMINOUS, UPPER CLARION, BUTLER, PA. (Bureau of Mines pretreated for Pyritic Sulfur Removal)										
RAW COAL		1.76	<0.20	<0.20	1.76				0.27	-
1	30	1.27	0.20	<0.20	1.26	28	-	28	-	0.44
1	60	1.16	<0.20	<0.20	1.16	34	-	34	-	0.90
1	120	1.28	<0.20	<0.20	1.28	27	-	27	-	1.18
PHS-398, RAW HEAD, 3A UPPER FREEPORT SEAM, SOMERSET, PA.										
RAW COAL		0.46	2.26	0.29	3.01	-	-	-	0.10	-
2	30	0.64	0.62	0.02	1.28	-40	73	57	-	0.14
2	60	0.63	0.19	0.04	0.87	-42	92	71	8.3	0.82
PSOC-108, HVB BITUMINOUS, PITTSBURGH, PA.										
RAW COAL		1.07	2.06	0.00	3.13	-	-	-	-	-
1	30	0.71	1.23	0.21	2.16	34	40	31	7.65	-
2	60	0.50	0.43	0.09	1.01	53	79	68	9.4	0.92
2	120	0.86	0.39	0.04	1.27	20	82	59	14.1	0.39
PSOC-342, HVA BITUMINOUS, CLARION, JEFFERSON, PA.										
RAW COAL		1.39	5.01	0.15	6.55	-	-	-	-	-
1	60	1.35	1.84	0.03	3.24	3	63	50	-	0.93
1	120	1.55	1.45	0.03	3.03	-11	71	54	12.83	0.15
MID-WESTERN COALS										
PSOC-190, HVA BITUMINOUS, ILL NO. 6, KNOX, ILL.										
RAW COAL		1.9	1.05	0.10	3.05	-	-	-	-	-
2	60	1.53	0.11	0.12	1.62	19	90	47	7.60	0.07
1	120	1.34	0.06	0.17	1.57	29	94	48	15.10	0.13

TABLE 3
Laboratory Coal Desulfurization Data
Eastern, Midwestern, Western Coals

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Ave. No. of Runs	Chlorination Time (Min.)	Residual Sulfur Analysis (Wt. %)				Sulfur Removal (%)			Dechlorination Residual Cl (Wt. %)	
		Organic	Pyritic	Sulfate	Total	Organic	Pyritic	Total	Before	After
PSOC-213, HVB BITUMINOUS, KY, NO. 9 ($CL_2(g)$ - 0.187 g/min.)										
RAW COAL		1.86	1.89	0.07	3.82	-	-	-	0.05	
1	120	0.53	1.65	0.01	2.19	72	13	43	4.6	0.57
PSOC-276, HVA BITUMINOUS, OHIO NO. 8, HARRISON, OHIO										
RAW COAL		2.24	2.07	0.84	5.15					
1	60	0.74	0.40	0.20	1.35	67	81	74	10.7	0.54
3	120	0.99	0.17	0.24	1.39	56	94	73	16.6	0.22
PSOC-026, HVC BITUMINOUS, ILL NO. 6, SALINE, ILL.										
RAW COAL		2.08	4.23	0.35	6.66					
1	30	1.30	0.89	0.02	2.21	38	79	67	-	0.20
1	60	1.25	0.55	0.06	1.87	40	87	72	8.46	0.42
WESTERN COALS PSOC-086, LIGNITE, ZAP, MERCER, NORTH DAKOTA										
RAW COAL		0.63	0.52	0.03	1.22				0.00	
1	30	0.35	0.23	0.17	0.75	44	59	39	-	0.33
1	60	0.32	0.35	0.06	0.73	50	37	39	8.00	-
PSOC-097, SUB-BITUMINOUS A, SEAM 80, CARBON, WYOMING										
RAW COAL		0.84	0.38	0.01	1.23					
1	30	0.70	0.31	0.05	1.06	17	18	14	-	0.28
1	60	0.74	0.05	0.02	0.81	12	87	34	-	0.13
1	120	0.79	0.19	0.06	1.05	5	50	15	-	0.22
PSOC-240, SUB-BITUMINOUS B, BIG D, LEWIS, WA.										
[illegible] COAL		1.75	1.60	0.01	3.36				0.02	
1	120	0.49	0.68	0.05	1.22	72	58	64	-	0.26

TABLE 3 (Cont'd)
Laboratory Coal Desulfurization Data
Eastern, Midwestern, Western Coals

Chlorination

Chlorination was carried out by bubbling chlorine at injection rates of 0.187 to 1.5 grams per minute through a slurry of 100 grams of -100 to + 200 mesh coals with 200 grams of solvent (methyl chloroform, carbon tetrachloride, tetrachloroethylene) and 20-70 grams of water contained in a 500 ml. stirred flask equipped with a reflux condenser, cold trap and gas holder, Figure 2. The chlorination was conducted at 50-100°C, atmospheric pressure and reaction times of 10, 20, 30, 60, and 120 minutes.

Observations indicated that chlorine injection rates of 0.187 grams per minutes were probably too low for obtaining maximum reaction rates. Chlorine injection at 1.5 grams per minute was excessive with chlorine being carried over from the coal slurry into the cold trap. At injection rates of 0.75 grams per minute, the injected chlorine was readily absorbed by the coal slurry with no penetration of the slurry surface until an apparent saturation limit for chlorine was reached at approximately 45 minutes. At this point, chlorine carryover into the vapor phase and cold trap suddenly becomes significant.

Sulfur analyses are reported for organic, pyritic, sulfate and total sulfur as obtained from Galbraith Laboratories. The attendant processing conditions for coal PSOC-219 are summarized in Table 2 for each product coal analyses. For the coal PSOC-219 chlorination data represented, retention time, chlorine injection rate, temperature, water content and solvent were variables with coal mesh size, and the solvent-to-coal ratio was kept invariant as noted in Table 2. Principal observations were that extended chlorination times above 60 minutes did not result generally in increased desulfurization.

Also, lower temperatures of 50 and 60°C and increased water/coal ratios of 0.7 resulted in decreased organic sulfur removal. Pyritic sulfur reduction may be favored by the lower temperatures of 50 to 60°C and reduced by the water to coal ratio of 0.7. The other 11 high sulfur eastern, midwestern and western coals were chlorinated with only retention time as a variable (30, 60, 120 minutes) and chlorine injection rate (0.75 gram/min.), temperature (74°C), solvent (methyl chloroform), solvent/coal (2), water/coal (0.5) and mesh size (-100 to +200) kept invariant.

Hydrolysis

Hydrolysis conditions were at water/coal ratios of 2, 3 and 4, with 1 and 2 washes and including a water/coal displacement wash of 1 and 2 in the 2 filtration steps for a total water/coal consumption between 4 and 10. Water temperatures were at 60°C, 80°C and 100°C as noted, Table 2. Hydrolysis times were generally 60 to 120 minutes and as low as 5-20 minutes for given tests. Tests with PSOC-219 indicated that a single water/coal wash at 2 at a wash time of 20 minutes and water temperature of 80°C reduced the sulfate concentration in the treated coal to less than 0.1 weight percent.

Dechlorination

Dechlorination conditions were at temperatures of 350 to 550°C in the presence of a steam atmosphere. Initial steam rates were high at 75-110 grams/hour with treated coal charged at 2-4 grams per batch. Reduction of steam values to 0.4 gram per hour have indicated no apparent reduction in the rate of HCl evolution in the dechlorination. At 450°C, the dechlorination appeared to be complete in under 20 minutes, Figure 5. The chlorine levels before dechlorination of the treated coal ranged from 4.6 to 24 weight percent and after dechlorination ranged from <0.01 to 1.29 weight percent.

COAL DESULFURIZATION CHARACTERIZATION

Twelve Eastern, Midwestern, Western Coals

A summary of organic, pyritic and total sulfur removal for 4 bituminous eastern coals, 5 bituminous midwestern coals, and 2 sub-bituminous and 1 lignite western coals is presented in Tables 2 and 3 (Kalvinskas, et. al. 1977). The data is representative of coal chlorination at a $Cl_2(g)$ feed rate of 0.75 gram/min -100 grams coal for 60 minutes. No specific correlations for sulfur removal exist with geographical region. Seven of the twelve coals show organic sulfur removal greater than 45 percent with a peak removal of 72 percent. Two coals show no or little organic sulfur removal. Nine of the twelve coals show pyritic sulfur removal between 58 and 92 percent. Total sulfur removals are between 34 and 74 percent for the 12 coals. The values represent averaged data. Individual runs and given sample analyses indicate peak removals at 83 percent organic sulfur, 99 percent pyritic sulfur and 83 percent total sulfur.

Total, organic and pyritic sulfur removals and residual sulfur concentrations after treatment by the desulfurization process are plotted against chlorination time for each of the twelve coals tested, Figures 6 to 11.

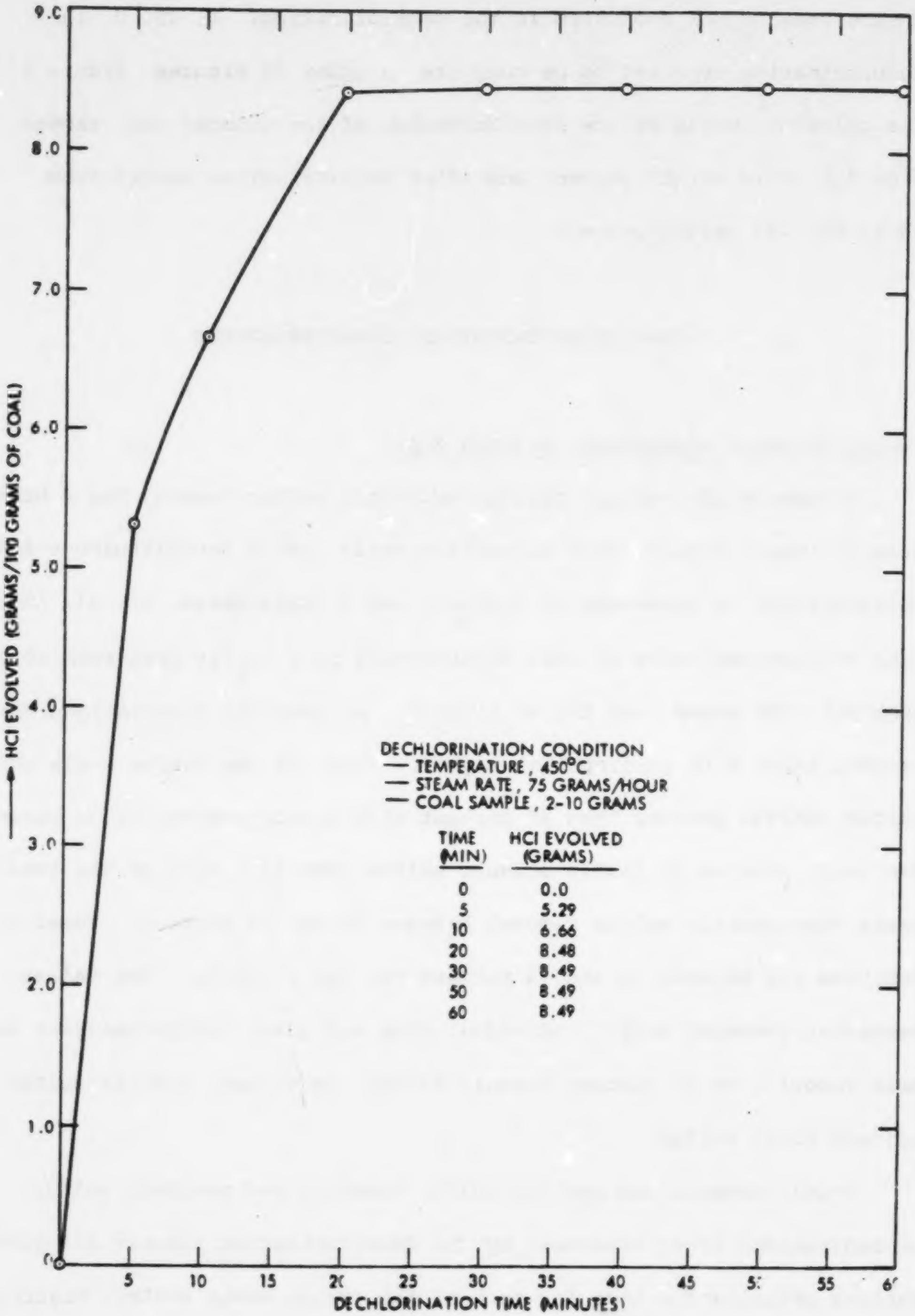


FIGURE 5. STEAM DECHLORINATION OF TREATED COAL WITH TIME

Total Sulfur

Total sulfur removal and residual total sulfur is depicted with chlorination time for 12 coals in Figures 6 and 7, respectively. Peak removals and minimum residual values are at 60 minutes chlorination time, which exceed sulfur removals at 30 and 120 minutes.

Organic Sulfur

Organic sulfur removals and residual organic sulfur for 12 coals is depicted with chlorination time, Figures 8 to 9. Residual organic sulfur values are grouped relatively high for coals PSOC-190, 342, 026, and 513, and represent an initially high organic sulfur in the raw coal that appears somewhat resistant to chlorination. Remaining coals have substantially reduced levels of organic sulfur with treatment for 60 minutes. Continual chlorination beyond 60 minutes to 120 minutes appears to increase organic sulfur values in 4 of the coals, and decrease organic sulfur in only 2 of the coals.

Pyritic Sulfur

Pyritic sulfur reductions and residual values with chlorination time are depicted, Figures 10 and 11, respectively. Pyritic sulfur shows a sharp reduction (44 to 48%, PSOC-219) at short reaction times of 10 to 20 minutes. Two of the coals, PSOC-219 and 097 have peak pyritic sulfur reduction of 78 and 87 percent at sixty minutes chlorination time and drop off to 65 and 50 percent at 120 minutes respectively. Four of the coals, PSOC-190, 276, 108, and 342, provide increasing pyritic sulfur removals beyond 60 minutes

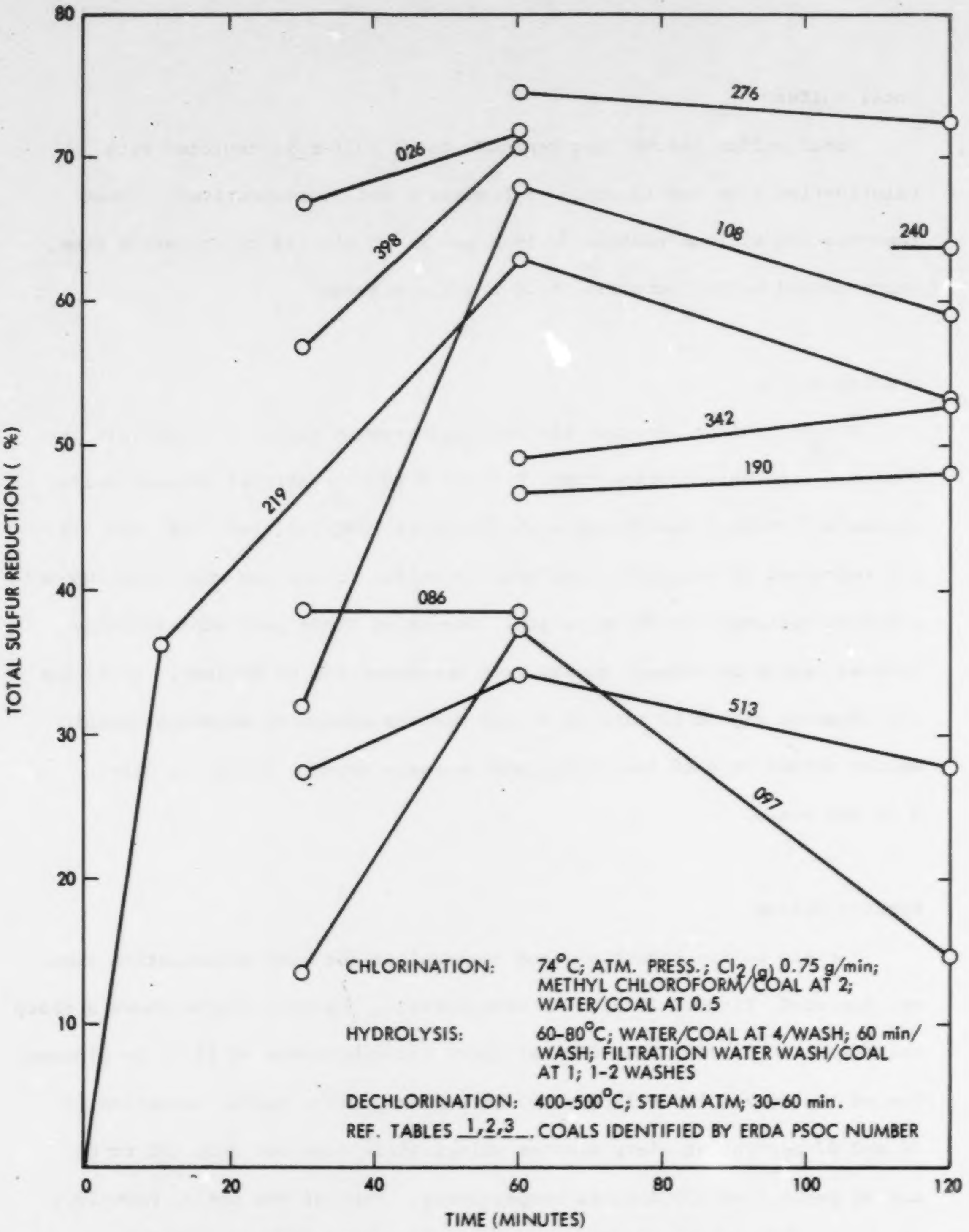


Figure 6, Total Sulfur Reduction with Chlorination Time (Eastern, Midwestern, Western Coals).

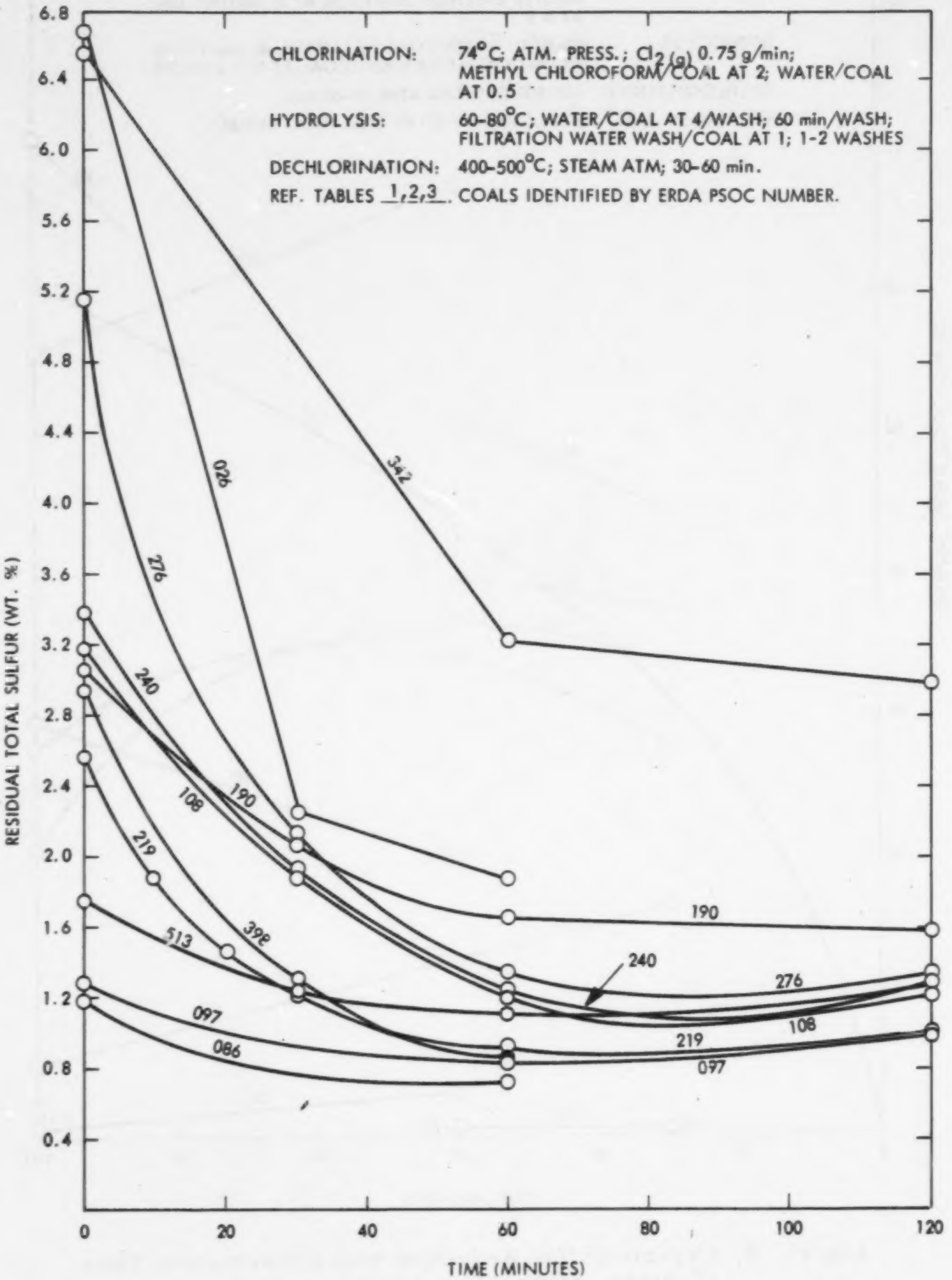


Figure 7, Residual Total Sulfur with Chlorination Time (Eastern, Midwestern, Western Coals).

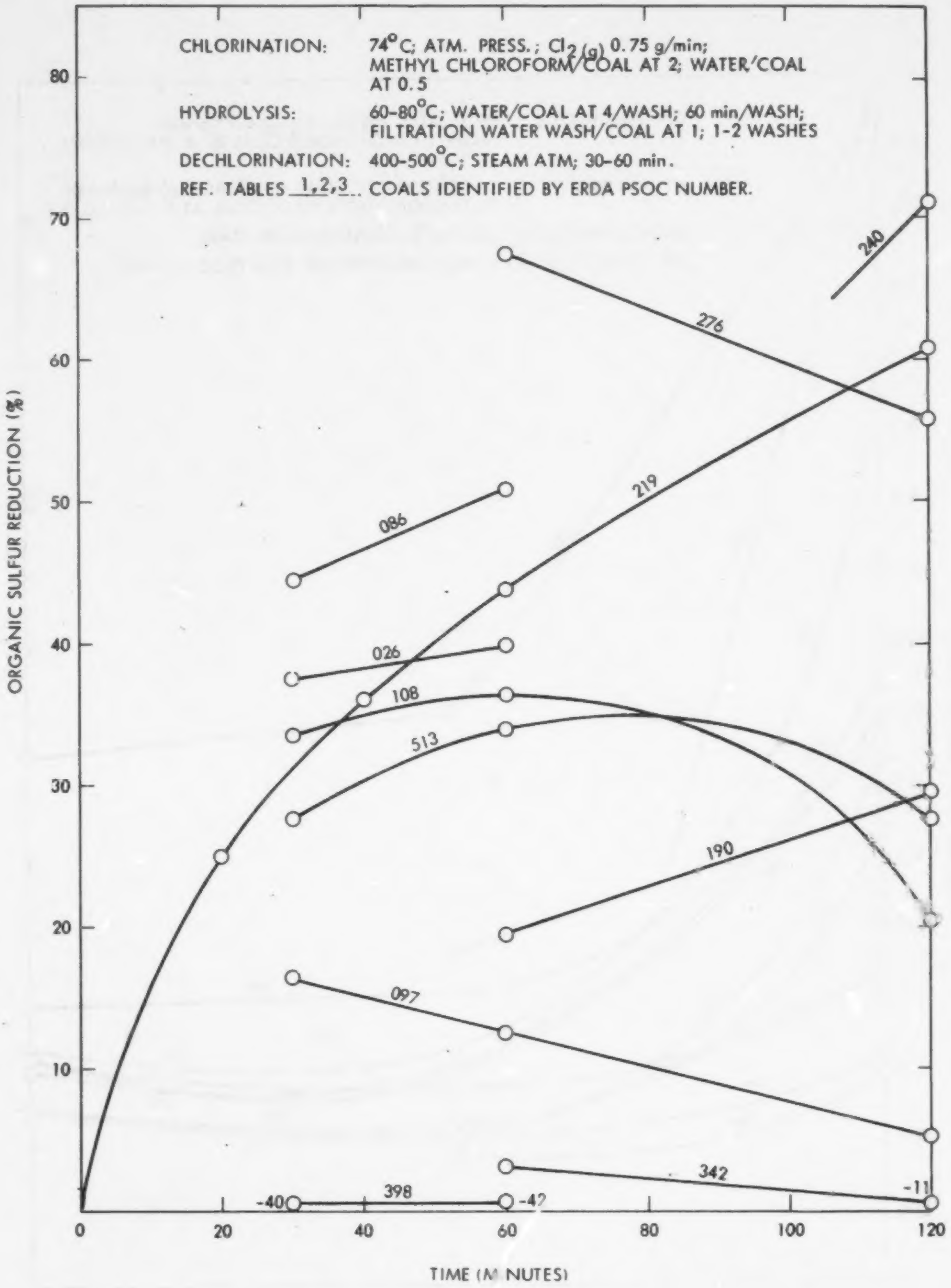


Figure 8, Organic Sulfur Reduction with Chlorination Time (Eastern, Midwestern, Western Coals).

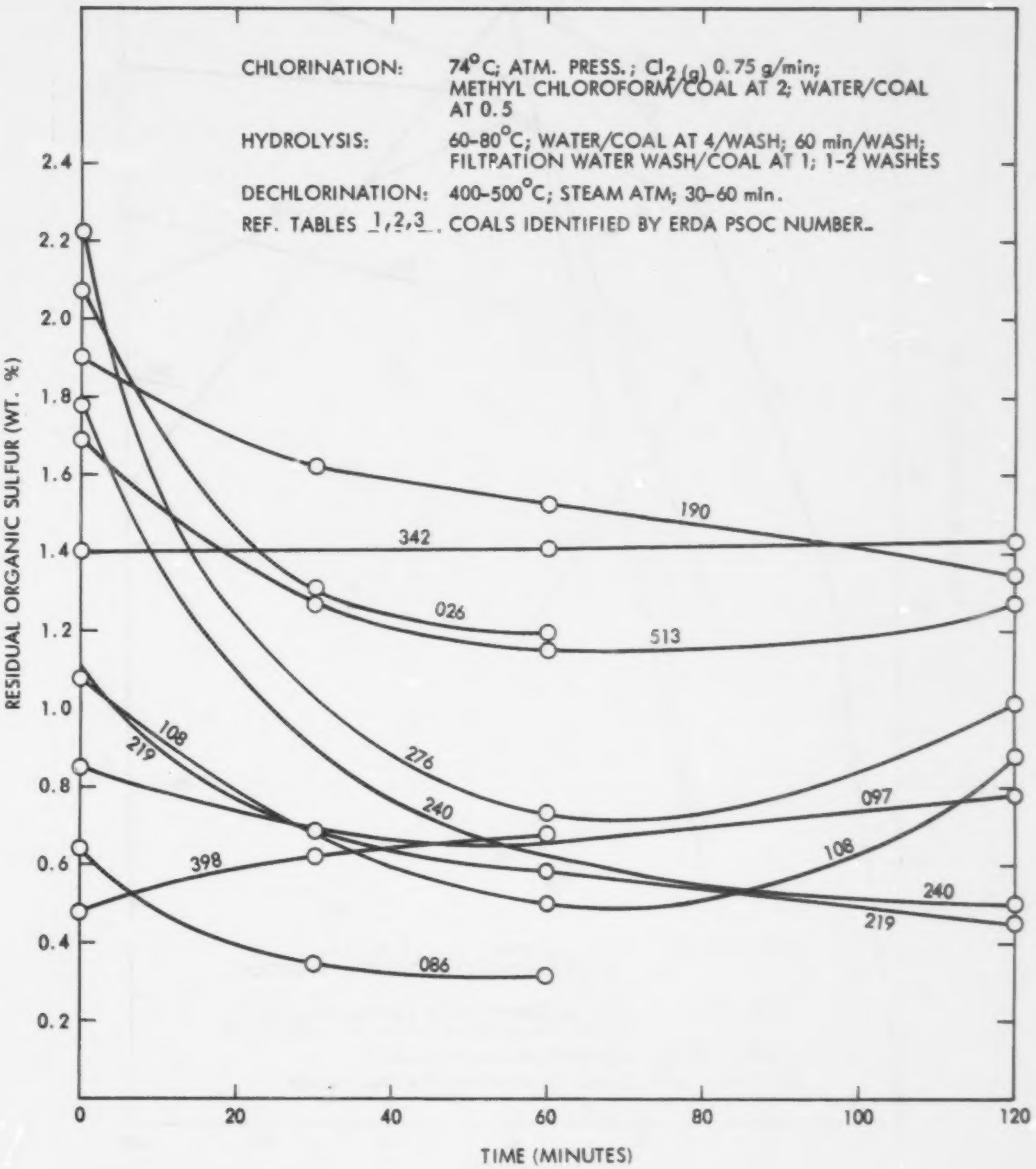
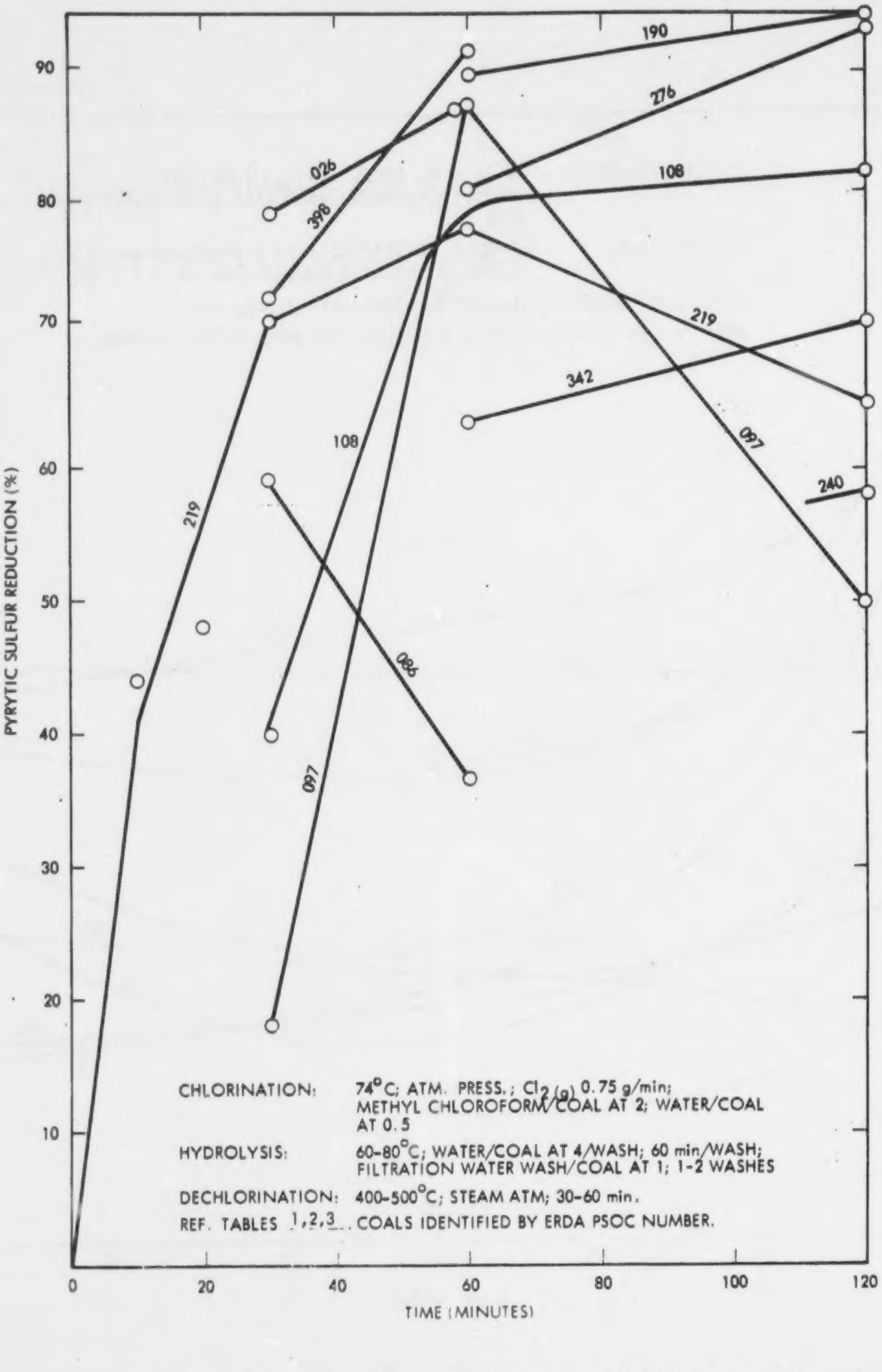


Figure 9, Residual Organic Sulfur With Chlorination Time (Eastern, Midwestern, Western Coals).



CHLORINATION: 74°C; ATM. PRESS.; $Cl_{2(g)}$ 0.75 g/min; METHYL CHLOROFORM/COAL AT 2; WATER/COAL AT 0.5

HYDROLYSIS: 60-80°C; WATER/COAL AT 4/WASH; 60 min/WASH; FILTRATION WATER WASH/COAL AT 1; 1-2 WASHES

DECHLORINATION: 400-500°C; STEAM ATM; 30-60 min.

REF. TABLES 1,2,3. COALS IDENTIFIED BY ERDA PSOC NUMBER.

Figure 10, Pyrytic Sulfur Reduction With Chlorination Time (Eastern, Midwestern, Western Coal).

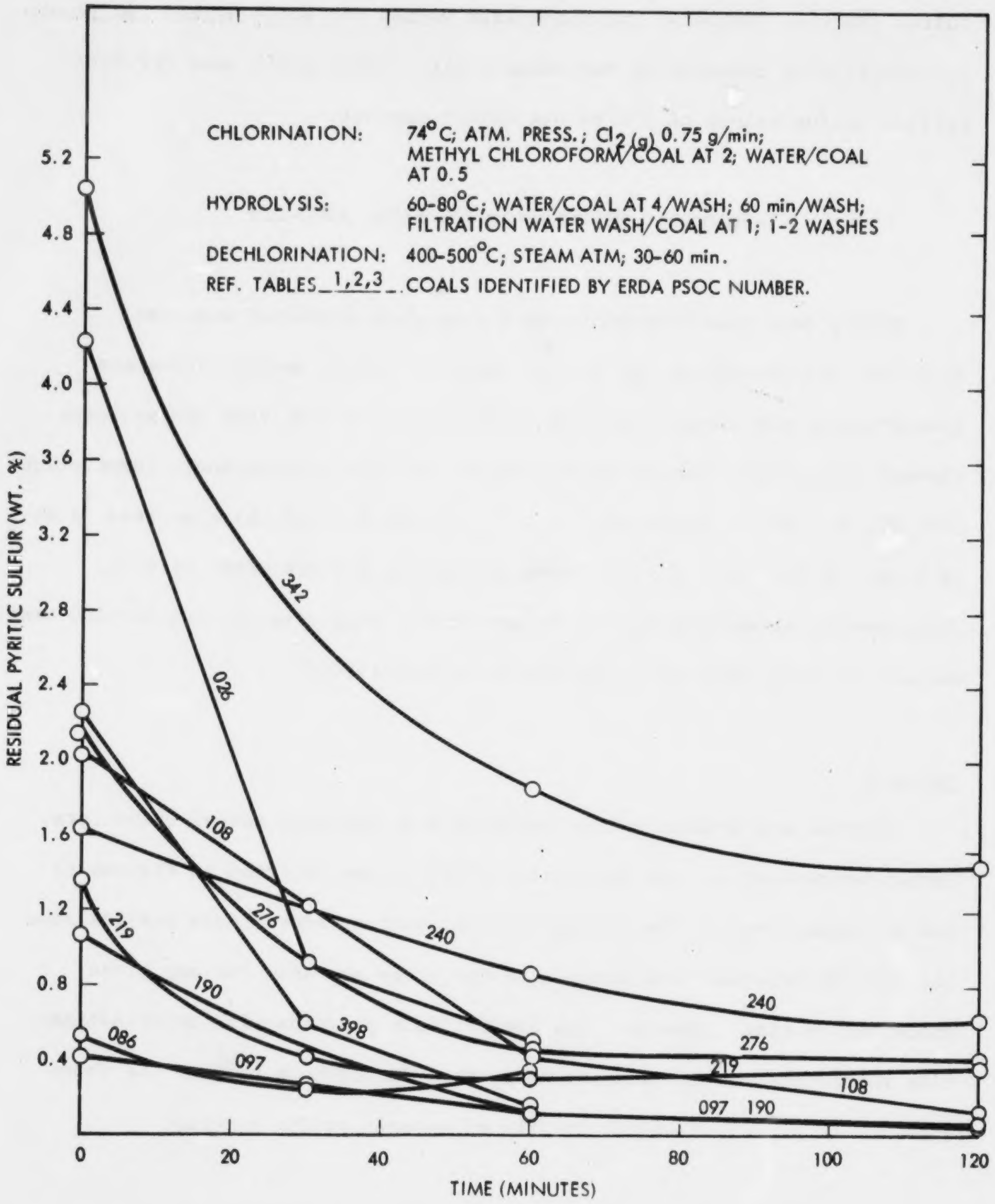


Figure 11, Residual Pyritic Sulfur with Chlorination Time (Eastern, Midwestern, Western Coals).

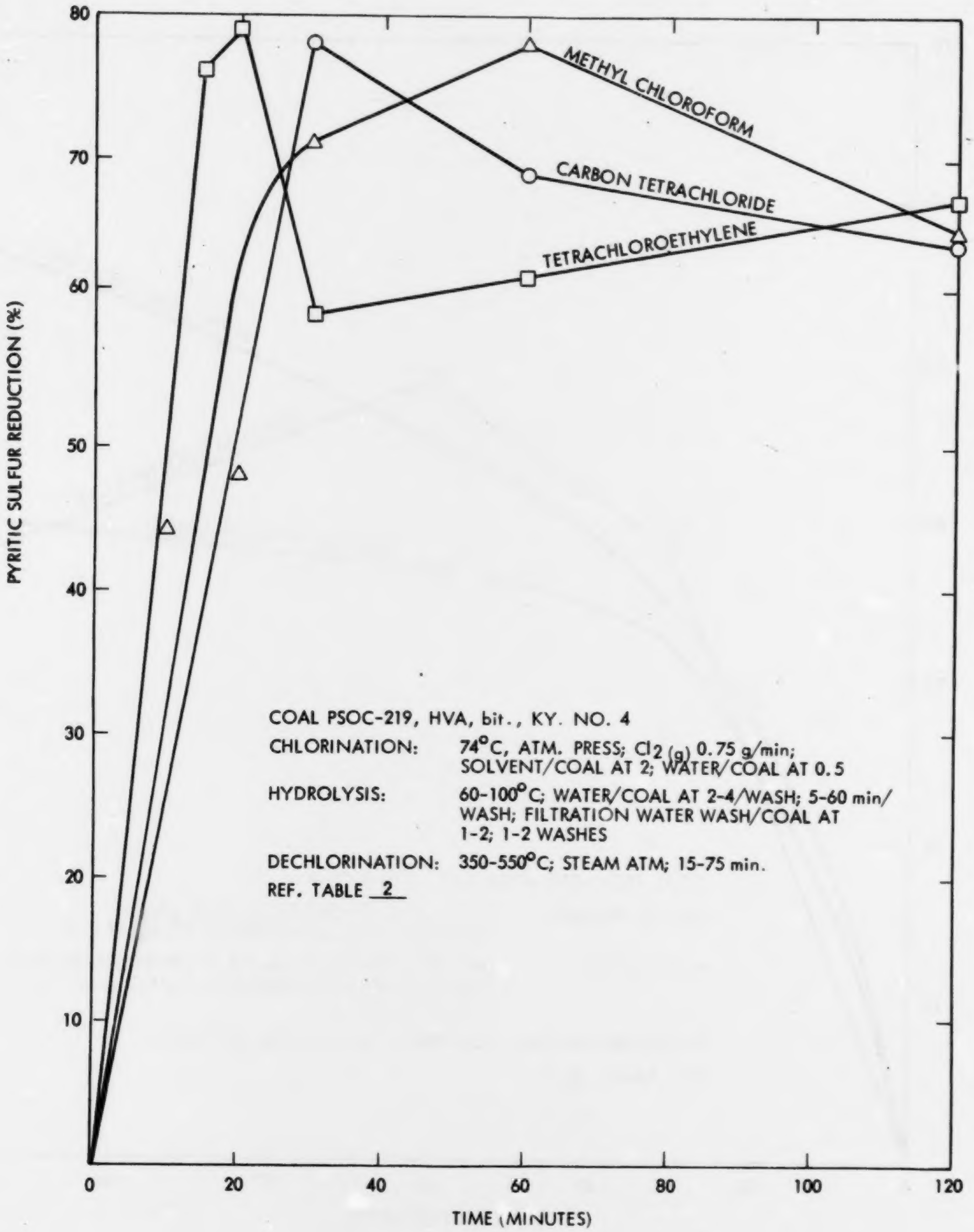
and up to 120 minutes. Analyses of given samples have shown up to 100% pyritic sulfur removal. Residual pyritic sulfur values for PSOC-342 and 240 remain relatively high compared to the other coals. Other coals have residual pyritic sulfur values of 0.1 to 0.4 weight percent.

PARAMETRIC DESULFURIZATION DATA, PSOC-219

Thirty coal desulfurization test runs were conducted with coal PSOC-219, HVA Bituminous Ky. No. 4, Table 2. Chlorination parameters investigated with respect to coal desulfurization with time are solvents (methyl chloroform, carbon tetrachloride, tetrachloroethylene), temperatures (50, 60, 74, 85°C), water/coal of 0.3, 0.5 and 0.7 and chlorine feed rates of 0.187, 0.375, 0.75 and 1.5 grams per minute per 100 grams of coal. Chlorination parameters kept invariant were: coal size at -100 to +200 mesh, solvent to coal ratio at 2, and atmospheric pressure.

Solvents

Pyritic and organic sulfur removals with solvents methyl chloroform, carbon tetrachloride, and tetrachloroethylene are depicted in Figures 12 and 13 respectively. The average pyritic sulfur removal data provide some distinct differences with respect to the three solvents for any given chlorination time. However, the overall data patterns with chlorination time represented do not suggest consistent differences between the three solvents in providing either pyritic or organic sulfur removal.



COAL PSOC-219, HVA, bit., KY. NO. 4

CHLORINATION: 74°C, ATM. PRESS; $Cl_{2\,(g)}$ 0.75 g/min; SOLVENT/COAL AT 2; WATER/COAL AT 0.5

HYDROLYSIS: 60-100°C; WATER/COAL AT 2-4/WASH; 5-60 min/WASH; FILTRATION WATER WASH/COAL AT 1-2; 1-2 WASHES

DECHLORINATION: 350-550°C; STEAM ATM; 15-75 min.

REF. TABLE 2

Figure 12, Pyritic Sulfur Reduction, Coal PSOC-219 with Chlorination Time (Parametric data with solvents - methyl chloroform, carbon tetrachloride, tetrachloroethylene).

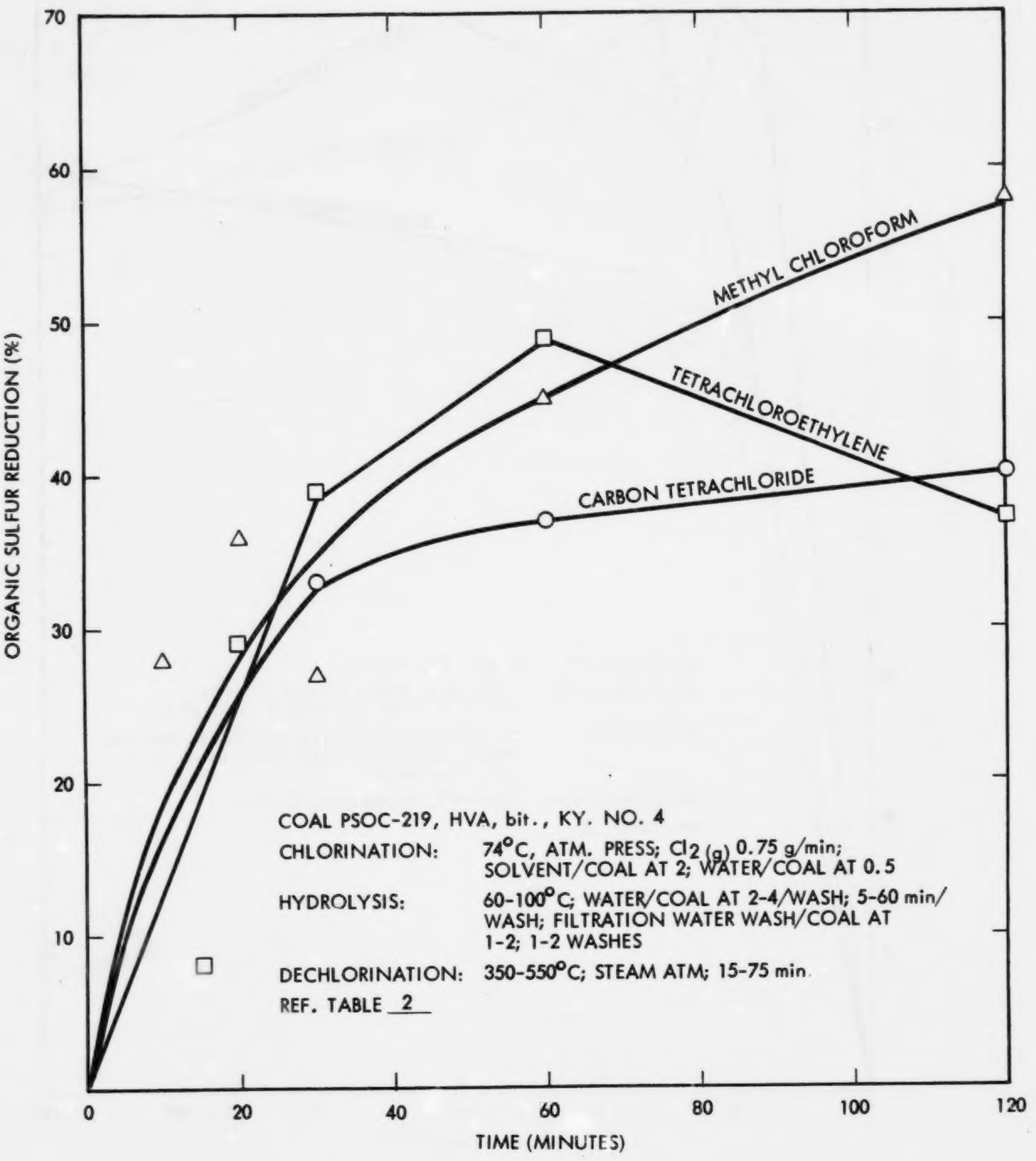


Figure 13, Organic Sulfur Reduction, Coal PSOC-219 with Chlorination Time (Parametric data with solvents - methyl chloroform, carbon tetrachloride, tetrachloroethylene).

Temperature

Pyritic and organic sulfur removal with chlorination time for chlorination temperatures of 50, 60, 74, and 85°C are depicted, Figures 14 and 15, respectively.

Pyritic sulfur removal appears aided by the temperatures of 50 and 60°C relative to 74°C and 85°C. Organic sulfur removal appears to be assisted by a temperature of 74°C relative to 50 and 60°C.

Water/Coal

Pyritic and organic sulfur removal with chlorination time is depicted for parameters of water/coal at 0.3, 0.5 and 0.7, Figures 16 and 17, respectively.

Although the overall patterns of data for water/coal with respect to chlorination time are not totally consistent, water/coal of 0.3 and 0.5 appear to favor greater pyritic and organic sulfur removal relative to a water/coal of 0.7.

Chlorine Feed Rates

Desulfurization data at low chlorine feed rates of 0.187 and 0.375 grams per minute per 100 grams of coal are available for comparision with the higher feed rates of 0.75 and 1.5 grams per minute per 100 grams of coal at long reaction times of 120 minutes, Table 2. There appear to be no significant differences in desulfurization data within the existing data variance between the different chlorine feed rates. At 30 and 60 minutes, there appears to be no advantage in desulfurization by increasing the chlorine feed rate from 0.75 to 1.5 grams/minutes - 100 grams coal.

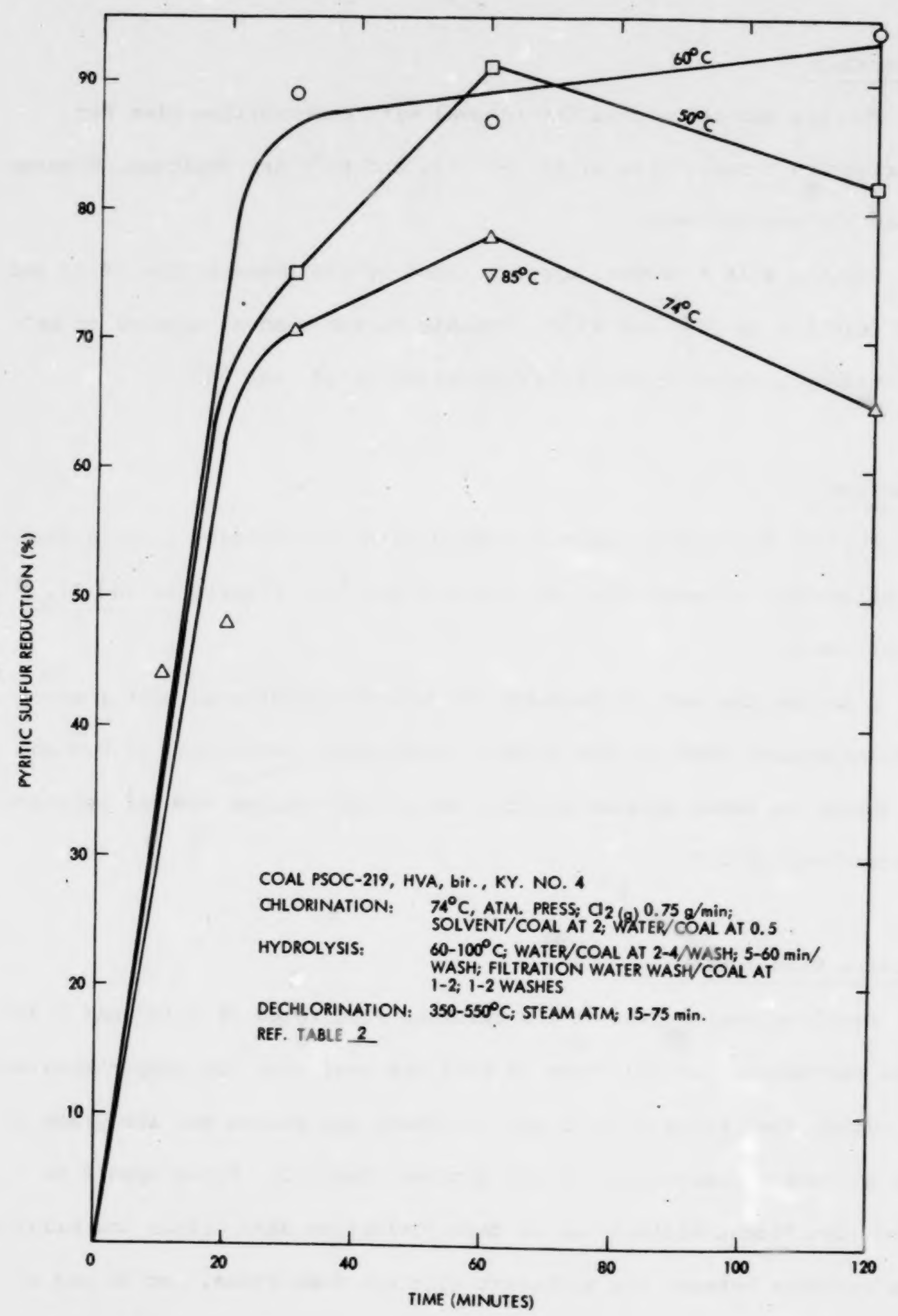


Figure 14, Pyritic Sulfur Reduction Coal PSOC-219 with Chlorination Time (Parametric values of temperature at 50, 60, 74, 85°C).

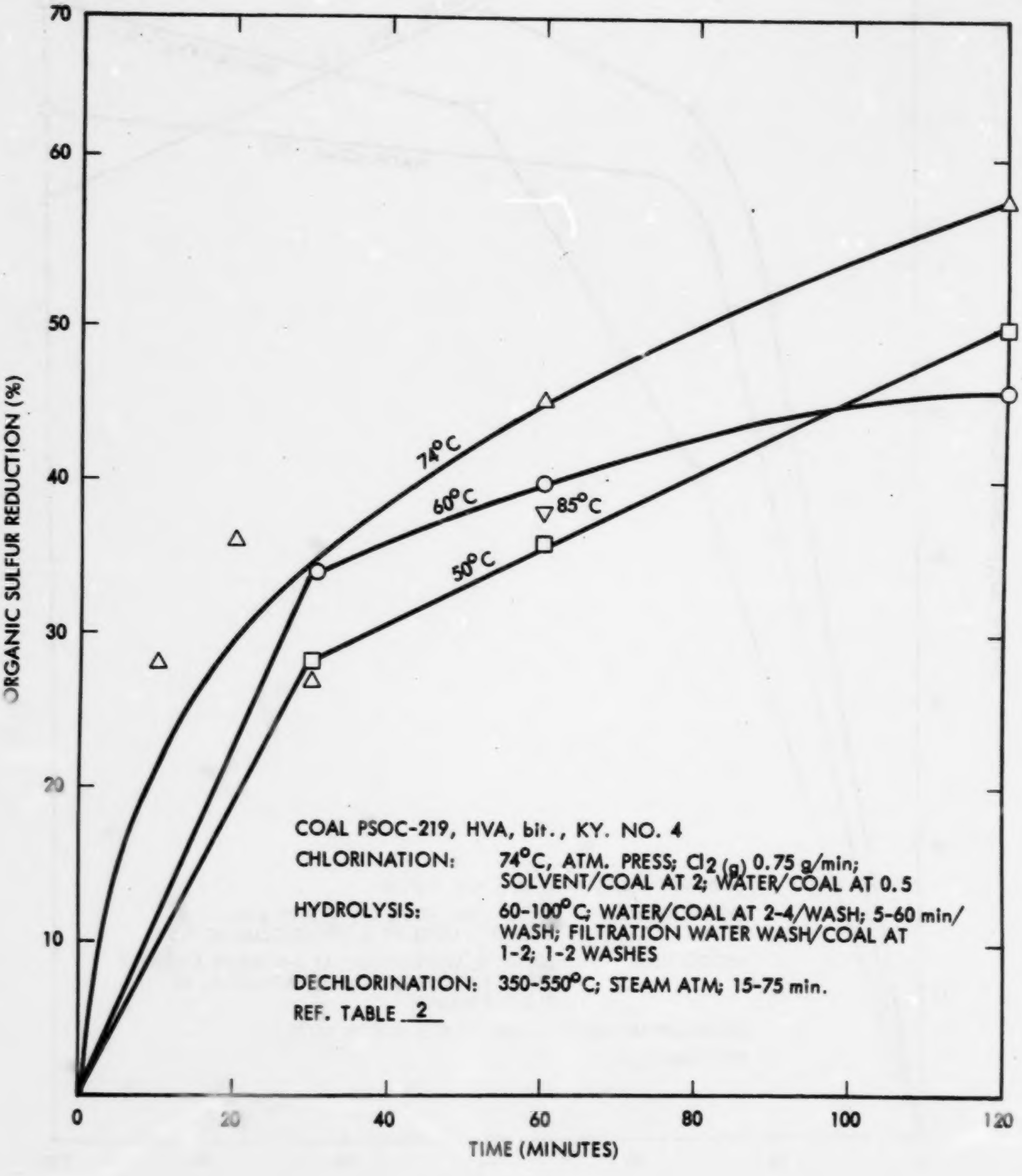
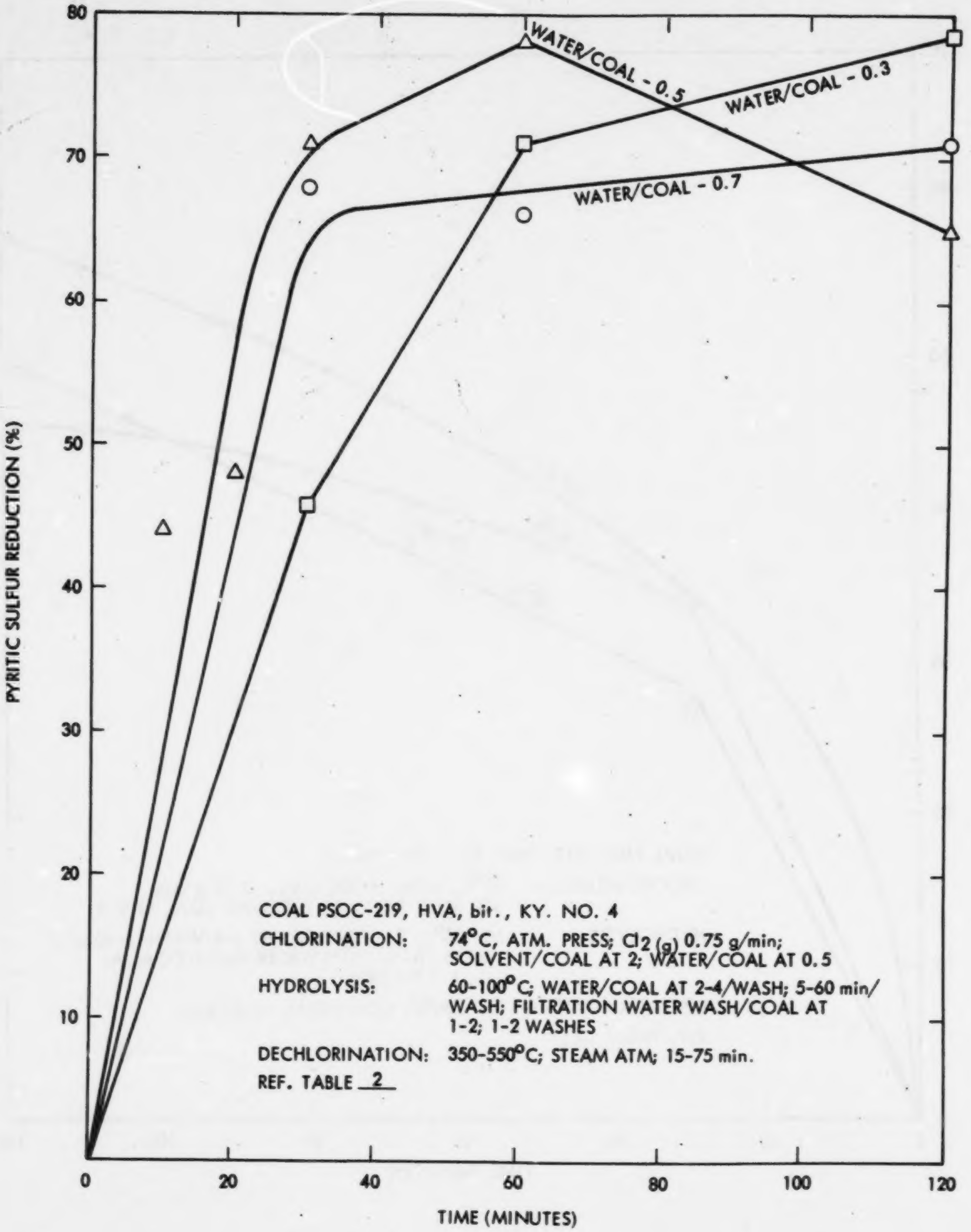


Figure 15, Organic Sulfur Reduction, Coal PSOC-219 with Chlorination Time (Parametric values of temperature at 50, 60, 74, 85°C)



COAL PSOC-219, HVA, bit., KY. NO. 4

CHLORINATION: 74°C, ATM. PRESS; $Cl_{2\,(g)}$ 0.75 g/min; SOLVENT/COAL AT 2; WATER/COAL AT 0.5

HYDROLYSIS: 60-100°C; WATER/COAL AT 2-4/WASH; 5-60 min/WASH; FILTRATION WATER WASH/COAL AT 1-2; 1-2 WASHES

DECHLORINATION: 350-550°C; STEAM ATM; 15-75 min.

REF. TABLE 2

Figure 16, Pyritic Sulfur Reduction, Coal PSOC-219 with Chlorination Time (Parametric values of water/coal at 0.3, 0.5, 0.7).

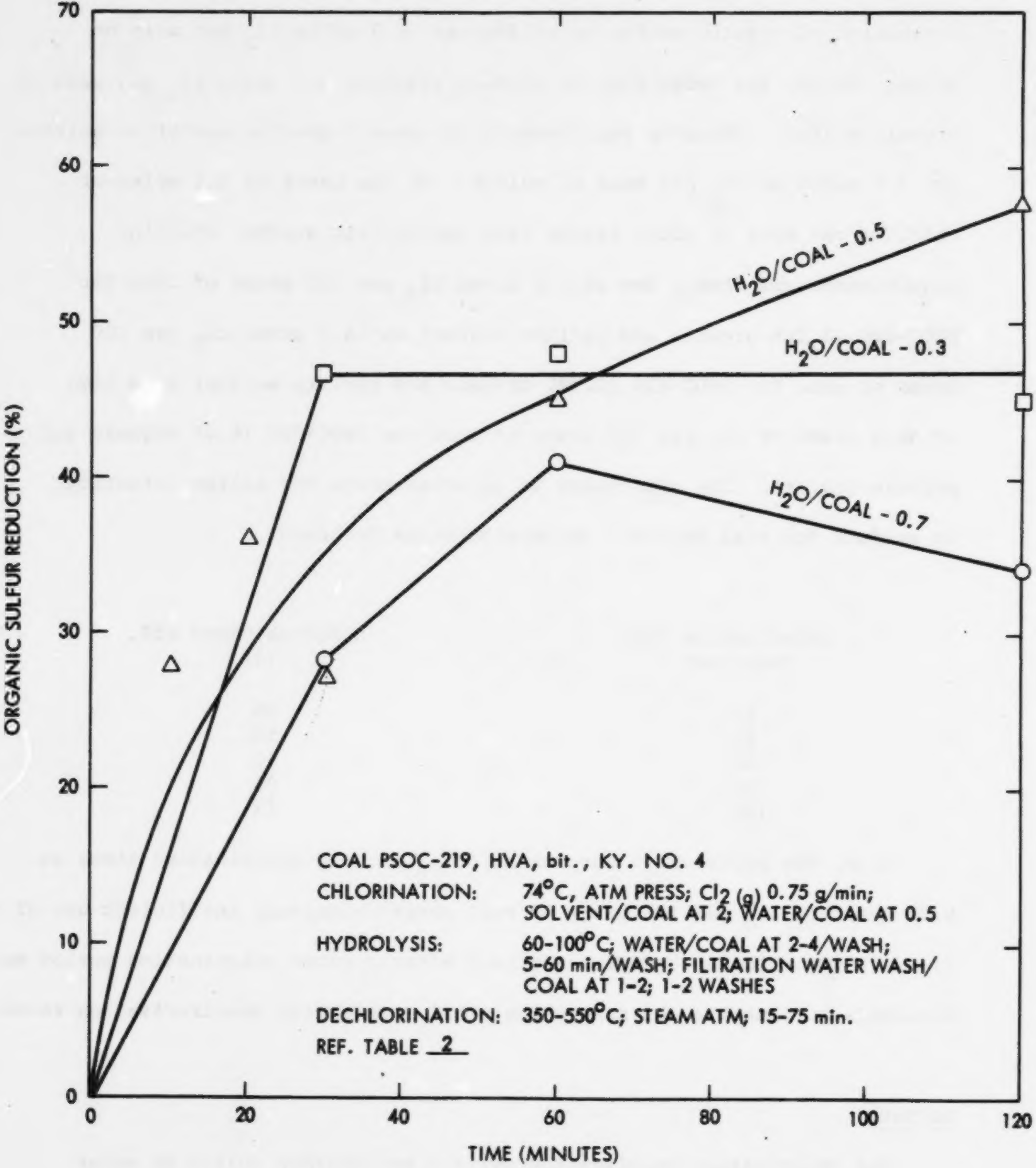


Figure 17, Organic Sulfur Reduction, Coal PSOC-219 with Chlorination Time (Parametric values of water/coal at 0.3, 0.5, 0.7)

A calculation of stoichiometric chlorine requirements for conversion of organic sulfur to sulfonates is 3 moles Cl_2 per mole of organic sulfur and conversion to sulfate requires 3.5 moles Cl_2 per mole of organic sulfur. Chlorine requirements to convert pyritic sulfur to sulfate are 3.5 moles of Cl_2 per mole of sulfur. On the basis of 3.5 moles of chlorine per mole of total sulfur less the sulfate sulfur, chlorine requirements are from a low of 9.2 grams Cl_2 per 100 grams of coal for PSOC-086 (1.19% organic and pyritic sulfur) to 19.2 grams Cl_2 per 100 grams of coal for PSOC-219 (2.48% organic and pyritic sulfur) to a high of 49.5 grams of Cl_2 per 100 grams of coal for PSOC-342 (6.4% organic and pyritic sulfur). The efficiency of chlorine usage for sulfur oxidation to sulfate for coal PSOC-219 appears to be as follows:

Chlorination Time (minutes)	Chlorine Usage Eff. (%)
10	95
20	54
30	40
60	26
120	12

Thus, the addition of surplus chlorine at long chlorination times at 0.75 g/min of Cl_2 per 100 grams of coal makes relatively inefficient use of chlorine. A reduction in chlorine addition after a short chlorination period may be desirable to conserve chlorine while still maintaining desulfurization rates.

Sulfate

The chlorination oxidizes the pyritic and organic sulfur to water soluble sulfates. Residual values of sulfate in the processed coal are primarily an indication of the effectiveness of the water wash in the hydrolysis stage and the displacement water wash in the filtration. Residual sulfate values for PSOC-219 are included in Table 2 and for the other 11 coals tested in Table 3. Sulfate values after washing are generally under 0.1 weight percent and only occasionally at higher values,up to 0.4 weight percent.

Generally excessive water wash conditions to extract the sulfate from the coal have been used. Preliminary data indicate that a single water wash at a water/coal of 2 in the hydrolysis stage at 80°C and 20 minutes followed by a water/coal filtration wash at 2/1 is adequate to reduce the sulfate content to less than 0.1 weight percent.

Residual Chlorine

Chlorine values in the treated coals before dechlorination range between 4.8 and 23.1 weight percent, Tables 2 and 3. The lower chlorine values are for the shorter chlorination times, 10 to 30 minutes, and the highest values are present at higher times of 60 to 120 minutes.

Dechlorination of the treated coal at temperatures of 350 to 550°C in a steam atmosphere for 15 to 75 minutes provides residual chlorine values from <0.01 to 1.29 weight percent with average values of less than 0.5 weight percent.

The bulk of the residual chlorine (95%) appears to be readily removed at even low temperatures of 350°C, low steam rates (steam to coal of 0.1) and 20 minutes. A number of dechlorination tests have shown reduced residual chlorine values of less than 0.1 weight percent.

Additional dechlorination experiments are required to obtain consistent dechlorination to 0.1 weight percent chlorine.

Ultimate Analyses

Ultimate analyses of raw and treated coals PSOC-219 and PSOC-190 are given in Table 4. Coal PSOC-219 exhibits a significant reduction in hydrogen, approximately 2 weight percent, whereas PSOC-190 exhibits less than 1 weight percent reduction in hydrogen. The nitrogen content in the PSOC-219 raw coal appears in error at 0.1 weight percent. The carbon content of PSOC-190 rises sharply after treatment, apparently as a result in part of the combined decrease (5.2 percent) of sulfur, oxygen and hydrogen.

Trace Metal

Trace metal analysis in raw/treated PSOC-219 and PHS-398 coals indicate sharp reductions for titanium, phosphorous, arsenic, lead vanadium, lithium and beryllium (Table 5). Reductions are from 48 to 91 percent in treated PSOC-219 coal.

Material Balance

Material balances were obtained for coal, methyl chloroform, chlorine and sulfur. Water solutions, cold traps and gas holders were sampled and analyzed to obtain total material balances. A material balance for run 118-9/9/77 on coal PSOC-219 is represented, Table 6. Solvent and chlorine balances are 98.6% and 94.1% respectively. Improvements in seals and handling should lead to a better recovery of solvent and chlorine. Coal losses are more substantial and reflect the fact that dechlorination was carried out with 2-4 gram samples. Relatively small handling losses of the coal in dechlorination of several tenths of a gram reflect sizeable percentage losses. Additionally, dechlorination in the run was carried out at 500°C which also provided a significant loss of volatile material. Restriction of dechlorination

Component	PSOC-219 (HVA Bit. KY No. 4)				PSOC-190 (HVA Bit. ILL. No. 6, Knox. Ill.)	
		Treated Coal				Treated Coal
	Raw Coal (Wt. %)	Run 138–10/17/77 (Wt. %)	Run 138–10/17/77 (Wt. %)	Run 120–9/16/77 (Wt. %)	Raw Coal (Wt. %)	Run 109–8/8/77 (Wt. %)
C	74.16	75.53	74.83	77.30	69.15	74.15
H	5.30	3.46	2.38	3.16	4.89	3.99
N	0.10	1.84	1.65	1.26	1.00	1.36
S	2.56	0.88	1.02	1.00	3.05	1.36
Cl	0.03	0.45	0.75	1.40	0.06	0.06
Ash	8.06	7.78	7.40	6.23	8.49	8.29
0 (by difference)	9.79	10.06	11.97	9.65	13.42	10.80
Moisture	0.00	–	–	0.00	0.00	–
Heating Value (Btu/lb)	13,398	12,412	12,780	–	–	–

Table 4. Ultimate analyses of treated coals PSOC-219 and PSOC-190

Analyses	PSOC-219[a] Raw Coal	PSOC-219 Treated Coal				PHS-398[b] Raw Coal	PHS-398 Treated Coal	
		Run 107 - 7/27/77		Run 120 - 9/16/77			Run 140 - 10/20/77	
	PPM	PPM	Percent Reduction (Wt. %)	PPM	Percent Reduction (Wt. %)	PPM	PPM	Percent Reduction (Wt. %)
Titanium	1086	510	53.0	680	37.4	1400	700	50.0
Phosphorous	131	68/130	48.1/0.8	68	48.1	1040	700	32.7
Arsenic	73	25	65.8	49	32.3	85	9	89.4
Lead	46	4	91.3	5	89.1	0.5	3	–
Vanadium	46	12	81.0	48	0.0	<25	<25	~0.0
Lithium	<10	5	~50.0	–	–	20	21	0.0
Barium	5	5	0.0	–	–	<10	92	
Beryllium	8	4	50.0	13	0.0	5	4	20.0
Cadmium	1	<1		–	–	–	–	–
Mercury	<1	<1		–	–	<0.5	<0.5	~0.0
Selenium	<1	<1		–	–	<1	<1	~0.0

[a] HVA Bit. Ky No. 4.

[b] Raw Head, 3A, Freidens (Somerset), Pa. Received from Dr. Scott R. Taylor, Bureau of Mines, Pittsburgh, Pa.

Table 5. Trace metal analyses of raw/treated PSOC-219 and PHS-398

Process Unit	Process Stream	Coal (Incl. Sulfur)		Methyl Chloroform		Chlorine		Sulfur	
		Grams	Wt. %	Grams	Wt. %	Grams	Wt. %	Grams	Wt. %
Chlorinator (Feed)	Coal, $C\ell$, Solvent, S	97.07		200		45		2.56	
Chlorinator Cold Trap	$CH_3CC\ell_3$, $C\ell$			1.3	0.7	12.69	28.2		
Chlorinator Gas Scrubber	$C\ell$, SO_4, TOC	0.045^c	0.046^c						
Chlorinator Gas Collector		0.0029	0.003						
Solvent Evaporator	$CH_3CC\ell_3$			195.8	97.9	1.5	3.3	<0.01^a	
Hydrolyzer	$C\ell$, SO_4, TOC,	1.1^c	1.1^c			18.1^b	40.2^b	1.30^a	50.8^a
	Trace Metals	1.125^e	1.16^e						
Dechlorinator Gas Scrubber	$C\ell$, SO_4, TOC	2.88^c	2.97^c			9.72^b	21.6^b	0.44^a	17.2^a
Dechlorinator Gas Collector		2.31	2.38						
Product Coal Storage	Product Coal, $C\ell$, S	74.09 (87.86)^d	76.33 (90.52^d)			0.34	0.8	0.71	27.7
Total Accounting		83.30	85.81	197.1	98.6	42.34	94.1	2.45	95.7
Unaccounted		13.77	14.19	2.9	1.4	2.66	5.9	0.11	4.3

[a] $SO_4^=$ as Sulfur

[b] Chloride

[c] Carbon

[d] Product Storage Including Unaccounted Coal

[e] Trace Metals

Table 6. Material balance for run 138-10/7/77, coal PSOC-219

temperatures to 400°C will bring losses on PSOC-219 to less than 1 weight percent. Losses of coal found prior to the dechlorination stage were ∿1.1 percent. The major handling loss and loss of volatile matter appeared to be in the dechlorination stage.

MINI-PILOT PLANT

Parallel with laboratory and bench-scale coal desulfurization studies, a continuous flow mini-pilot plant will be constructed for an integrated equipment operation. Coal will be fed at a nominal rate of 2000 grams per hour from a pulverized coal feed hopper through chlorination, hydrolysis and dechlorination stages. The coal desulfurization mini-pilot plant is represented as an integrated equipment unit, Figure 18.

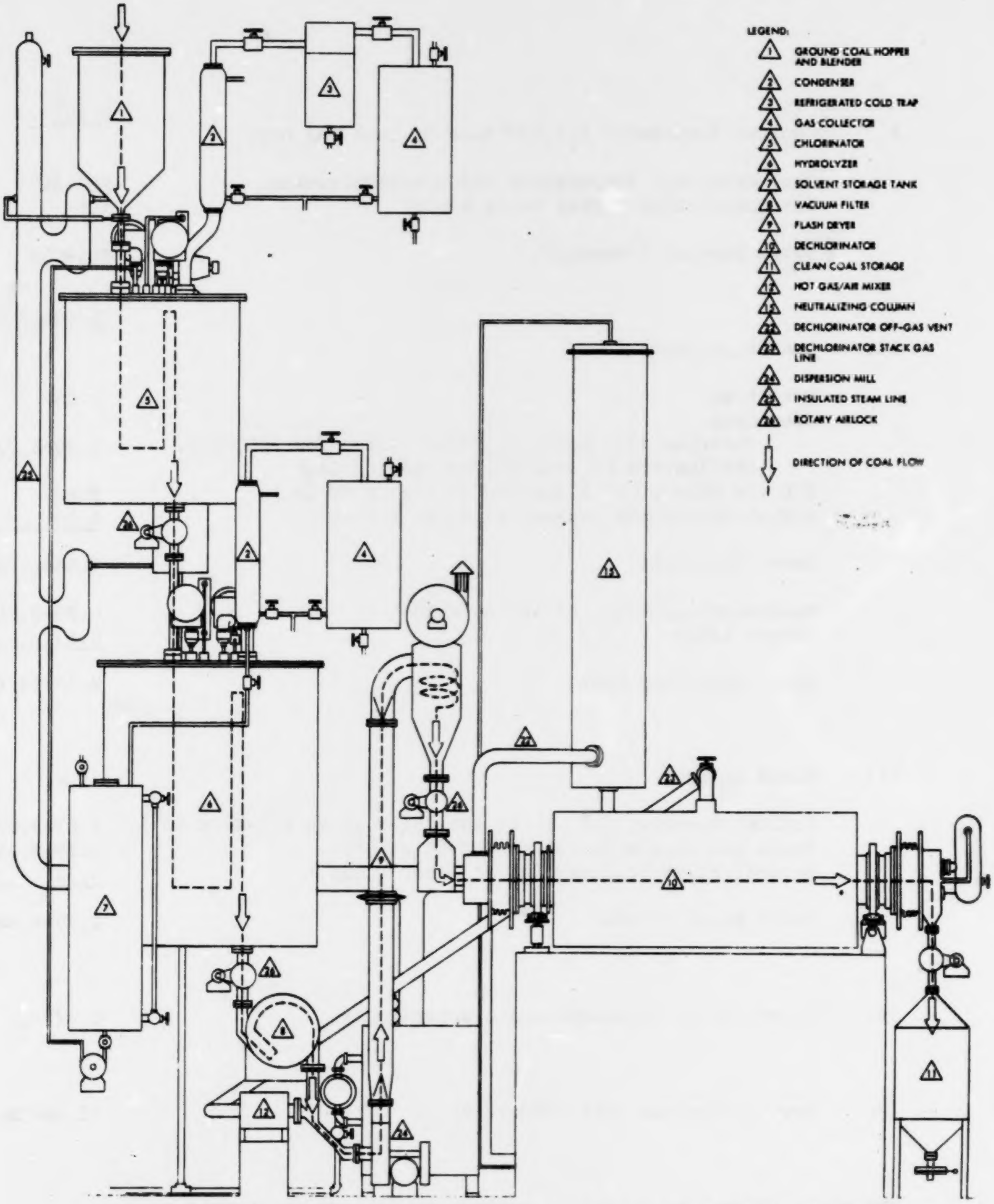
Major equipment units include a ground coal hopper and blender, chlorinator, hydrolyzer, rotary vacuum filter, flash dryer, dechlorinator and product coal storage hopper.

The chlorinator and hydrolyzer will be constructed of acid-resistant brick in lieu of more expensive metal claddings. An immersion testing program has been conducted with the assistance of Pennwalt Corporation and Stebbins Engineering and Manufacturing Co. to choose acceptable brick and mortar samples for the highly corrosive and abrasive conditions to be found in the chlorinator and hydrolyzer.

ECONOMICS

Capital Costs

Preliminary cost estimates have been made (JPL, 1976) for a 12,500 ton per day coal processing plant, Table 7. The capital costs for the coal preparation and desulfurization plant are estimated at $23-46 million. On the basis of capital costs provided (L.E. Bostwick, 1977) a grass roots Kel-chlor plant for conversion of HCL to Cl_2 is $62 million. The total capital investment is estimated at $84-108 million.



DRAWING NO. 345-800-A

NOTE: SCALE FOR ORIGINAL 18 X 21 DRAWING SCALE 17/32" = 1'

Figure 18. JPL coal desulfurization mini-pilot plant -- side elevation

I.	Capital Investment (12,500 Tons of Coal Per Day)	$ 10^6
	Coal Handling, Preparation and Desulfurization	$23-46
	Kel-Chlor Plant (Grass Roots Basis)	$62
	Total Capital Investment	$85-108
II.	Operating Cost	($/ton)*
	Utilities	1.05
	Materials	
	Chlorine (3.5 Moles Cl_2/Mole Sulfur for PSOC-219, 384 lbs/ton of coal @$17-35/ton of Cl_2)	3.26-6.71
	HCL (5% makeup, 19.2 lbs/ton of coal @ 3¢/lb.)	0.58
	Methyl Chloroform (Makeup at 0.5%, 20¢/lb.)	4.00
	Total Materials	7.84-11.29
	Maintenance (5%/yr. of $23-46 x 10^6)	0.28-0.56
	Direct Labor	0.55
	Total Operating Cost	9.72-13.45
III.	Fixed Charges	
	Capital Recovery (15 yr. at 10% Interest at $23-46 x 10^6)	1.81-3.62
	Taxes and Insurance (3% of $23-46 x 10^6)	0.17-0.34
	General Plant Expense (80% of Labor + Sup.)	0.72
	Total Fixed Charges	2.70-4.68
IV.	Waste Stream Treatment and Disposal Costs	0.92
V.	Overall Process Cost (PSOC-219)	13.34-19.05

*Multiply ($/ton) by 1.1025 to convert to dollars per metric ton.

Table 7. Preliminary cost estimate for coal desulfurization of 12,500 tons per day of PSOC-219 coal.

Operating Costs

The largest portion of the operating costs are raw material costs. Chlorine costs have been included on the basis of the stoichiometric amount of Cl_2 required to oxidize the organic and pyritic sulfur contained in PSOC-219 coal to sulfate. The Cl_2 requirement is 384 lbs. per ton of PSOC-219 coal. A cost of \$17 to \$35/ton of Cl_2 includes all operating costs and capital charges. The \$17 per ton of Cl_2 represents an early published cost (Van Dijk and Schreiner, 1973) based on a battery limits plant and the \$35 per ton of Cl_2 represents a recent estimated cost for a grass roots plant (Bostwick, 1977). Methyl chloroform solvent costs are based on a 0.5% process loss. The cost of methyl chloroform is estimated on the basis of cost projections for large scale production. A reduced solvent usage requirement or improved solvent recovery will have a significant impact in cost reduction. Capital and maintenance charges are called out only for the coal processing plant since Kel-Chlor charges have been included in the chlorine cost.

Fixed Charges

Capital recovery of the coal processing plant has been estimated on the basis of 15 years at 10% interest charges. Taxes and insurance are 3% of the fixed capital investment. Total fixed charges amount to \$2.70-4.68 per ton of coal.

Waste Stream

Earlier cost estimates have assumed that sulfuric acid recovery as a by-product would defray the waste steam processing costs. Until this is substantiated, an additional charge of \$0.92 per ton of coal has been included for waste treatment and sludge processing. It's based on a sludge processing cost with no by-product recovery and is in line with sludge disposal costs incurred in flue gas desulfurization (Jimeson and Maddocks, 1976).

Overall Process Costs

The overall process costs for coal PSOC-219 are estimated at $13.34 to $19.05 per ton of coal feed. Coals with higher or lower sulfur content will have a proportionately higher or lower processing cost based on the chlorine requirement of 3.5 moles per mole of organic and pyritic sulfur. The chlorine cost amounts to $1.55-2.94 for each 1 weight percent of sulfur in the coal. Any inefficiencies in the chlorine usage in the process will be reflected in proportionately higher chlorine costs.

RESULTS AND CONCLUSIONS

Coal desulfurization data for twelve eastern, midwestern and western coals that include bituminous, sub-bituminous and lignite coals show substantial organic and pyritic sulfur removal for the majority of coals, Table 8. Five coals show greater than 50% organic sulfur removal, 5 coals show better than 80% pyritic sulfur removal and 6 coals show better than 60% total sulfur removal. No correlation appears between sulfur removal and geographical origin of the coal. The desulfurization process appears applicable to a wide variety of coals. Optimization of the coal desulfurization process operating conditions is expected to achieve desulfurization levels required to meet environmental sulfur compliance levels for a substantial number of coals. Costs of the desulfurization process are competitive with existing flue gas desulfurization processes and other chemical coal cleaning processes for desulfurization.

COAL DESCRIPTION	SULFUR REMOVAL (%)		
	ORGANIC	PYRITIC	TOTAL
EASTERN COALS			
PSOC-108, HVA Bit. Pittsburgh, Wash., PA.	53	79	68
PSOC-342, HVA, Bit. Clarion, Jefferson, PA.	3	63	50
PHS-398, Raw Head, 3A Upper Freeport, Somerset, PA. (BOM-High Pyr., Low Org.)	- 42	92	71
PHS-513, Mine 513, Upper Clarion, Butler, PA. (BOM-Phys. Cleaned, High Org.)	34	-	34
MIDWESTERN COALS			
PSOC-219, HVA Bit. Ky #4, Hopkins, Ky.	45	78	63
PSOC-276, HVA Bit. Ohio #8, Harrison, Ohio	67	81	74
PSOC-026, HVC Bit. Ill. #6, Saline, Ill.	40	87	72
PSOC-213, HVB Bit. Ky. #9 (120 min., Cl_2(0.182 g/min)	72	13	43
PSOC-190, HVA Bit. Ill. #6, Knox, Ill.	19	90	47
WESTERN COALS			
PSOC-240A1, Sub-bit. B Big D, Lewis, Wash. (120 Min.)	72	58	64
PSOC-097, Sub-bit. A Seam 80, Carbon, Wyo.	12	87	34
PSOC-086, Lignite Zap. Mercer, N. Dak.	50	37	39

*(Chlorination - 60 minutes, Cl_2 @ 0.75 g/min. - 100 grams)

Table 8. Summary of Coal Desulfurization Data*
Eastern, Midwestern, Western Coals

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ACKNOWLEDGEMENT

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Conversion factors from English units to the International System of Units (ISU)

To convert from English units	to ISU	multiply by
atmosphere	newton/meter^2	1.01325 x 10^5
British thermal unit (mean)	joule	1.05587 x 10^3
inch	meter	2.54 x 10^{-2}
pound (lbm avoirdupois)	kilogram	4.5359237 x 10^{-1}
ton (short, 2000 pound)	kilogram	9.0718474 x 10^2
ton (metric)	kilogram	1.00 x 10^3

OXIDATIVE COAL DESULFURIZATION USING NITROGEN OXIDES - THE KVB PROCESS

E. D. Guth
KVB, Inc.
Tustin, California

ABSTRACT

The ecologically acceptable utilization of coal energy sources is vital to the nation's technological progress and economic well being. Methods and processes to control coal combustion emissions particularly sulfur oxides are being evaluated to determine their relative merits. KVB's coal desulfurization process offers a low cost means to remove pyritic and up to 40 percent of the organic sulfur from coal.

The KVB coal desulfurization process is based upon selective oxidation of the sulfur constituents of the coal. In this process, dry coarsely ground coal (+28 mesh) is heated at one atmosphere pressure in the presence of nitrogen oxide and oxygen gases for the removal of a portion of the coal sulfur as gaseous sulfur dioxide (SO_2). The remaining reacted sulfur in the coal is in the form of inorganic sulfates, sulfites or is included in an organic radical. The non-gaseous sulfur compounds derived from pyrites are removed from the pretreated coal by subsequent washing with water. Additional washing with heated caustic solution followed by water removes up to 40 percent of the organic sulfur.

The active oxidizing agent is believed to be NO_2. The process, however, uses a gas mixture containing oxygen (0.5 to 20 percent O_2 by volume), nitrogen monoxide (0.25 to 10 percent NO by volume), nitrogen dioxide (0.25 to 10 percent NO_2 by volume) and nitrogen (N_2) the remainder.

The mechanism of oxidation is not known; however, it is postulated that NO is oxidized by oxygen to NO_2 which is reduced back to NO in the reaction to form oxidized sulfur compounds.

The process is in its early stages of development. Laboratory experiments conducted on 50 gram samples in a batch reactor, with five different coals, indicate that the process has desulfurization potential of up to 63 percent of sulfur with basic dry oxidation plus water washing treatment and up to 89 percent with dry oxidation followed by water washing, caustic treatment and final water washing. However, depending on the amount of desulfurization required, the extraction and washing steps may or may not be

required. Where dry oxidation only could remove sufficient sulfur to meet the sulfur dioxide emission standards, this technology provides a very simple and inexpensive system.

The washing step removes iron and loosely bound inorganic material which reduces the ash content of the coal.

In the KVB process all the pyritic sulfur is converted to either sulfur oxides or sulfates.

Economic estimates indicate that coal could be desulfurized on a commercial scale for $6.00 to $10.00/ton using KVB's process.

INTRODUCTION

Chemical coal cleaning is the treatment of coal with chemical reactants to produce a product with improved more uniform fuel properties. The purpose of chemical coal cleaning is sulfur removal. Also minerals and trace elements are removed in the processing steps. Precombustion desulfurization can decrease the need for flue gas scrubbers as well as reduce corrosion in power generating units using coal as the fuel. Off-line coal desulfurization increases the reliability of power unit operation by reducing boiler dependence on scrubber operation. The decrease in ash and trace elements has the added advantages of decreased mill wear, less fuel and ash to transport and more uniform combustion properties. In evaluating coal cleaning the overall power plant fuel scenario should be examined considering the advantage of R.O.M. and processed fuels. Lower corrosion will lead to lower capital and operating costs. Ash and trace element contaminants are removed from the flue gas by physical methods (e.g., precipitators).

KVB's chemical coal cleaning method is part of an overall fuel cleaning technology. Since 1973 KVB has developed fuel cleaning technology to remove sulfur from oils and coal. This presentation is a report on the technical development of KVB's coal desulfurization method. Some aspects of the oil desulfurization technology are discussed as they relate to the removal of organic sulfur from coal.

The selective oxidation of the sulfur compounds in coal is the primary step of KVB's patented (U.S. 3,902,211) coal desulfurization process. The oxidation uses gas phase nitrogen dioxide as a carrier for oxygen with nitrogen as a diluent and removes sulfur in three ways (Figure 1):

- Gas Phase - oxidizing about one half of the pyritic sulfur to SO_2
- Water Phase - washing the oxidized pyritic sulfur from the coal as water soluble iron sulfites and sulfates
- Caustic Phase - treating the water washed coal with caustic to remove about one half of the organic sulfur as inorganic sulfites and sulfates

The three sulfur removal steps can be employed singly or in combination with or in conjunction with other methods for physical removal of pyritic sulfur.

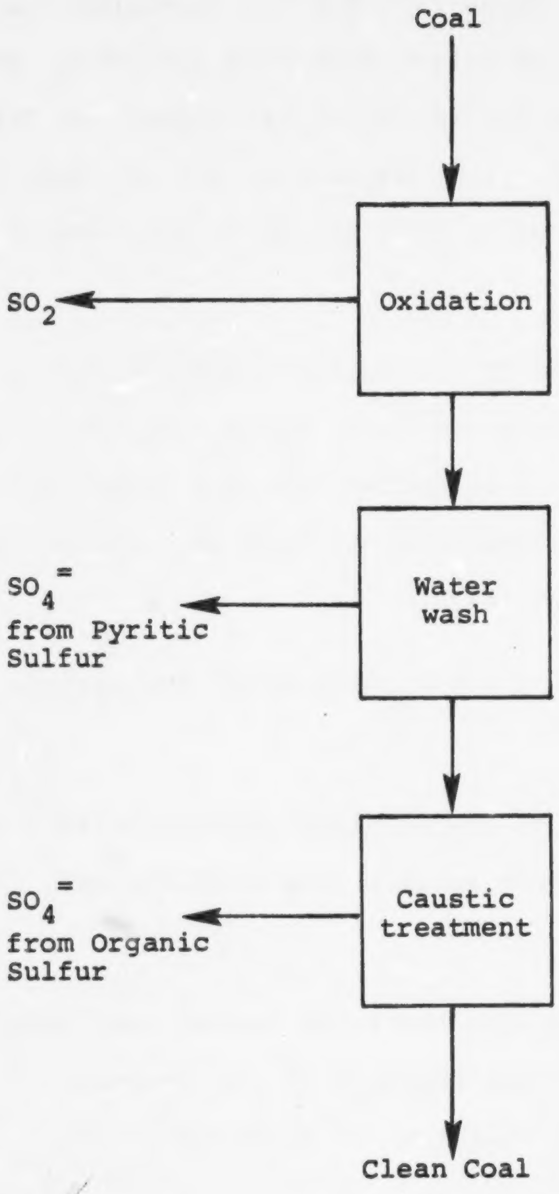

Figure 1. Process description.

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The oxidation of organic sulfur compounds to sulfides and sulfones using NO_2 and oxygen is reported in the patent literature. The NO_2 oxidation can be carried out to oxidize the sulfur atoms selectively. Further, reactant NO_2 is regenerated from the reduced form, NO, by reaction with gaseous oxygen at ambient conditions. KVB has applied NO_2 oxidation to the complex mixtures of inorganic and organic chemical forms of sulfur in oil and coal for sulfur removal.

The high oxidation potential of NO_2 and its selectivity of reaction to oxidize sulfur compounds make possible the use of mild oxidation conditions. The oxidation operation in KVB's coal desulfurization process is carried out at atmospheric pressure and temperatures up to 100 °C. Coarse ground coal can be used (-14 +28 mesh) as the oxidizing gas penetrates the coal structure.

KVB's coal desulfurization technology is in the early stage of development and has the potential for a low cost chemical coal cleaning method; however, there are still questions to be answered. This presentation covers the reaction conditions and laboratory test results for the three types of sulfur removal, oxidation, water wash, caustic wash, the chemistry of the sulfur reactions, including a discussion of organic sulfur reactions and preliminary process economic estimates.

Reaction Conditions

Ideally a chemical coal cleaning process would have the following characteristics:

- Coal size - coarse (+ 28 mesh)
- Temperature - low (ambient to 100 °C)
- Pressure - atmospheric
- Efficiency - pyritic sulfur (90-100% removal)
  - organic sulfur (90-100% removal)
- Chemical usage - small quantity, low cost
- Selectivity - no adverse changes in the coal
- Process time - short (1-15 minutes)

KVB's chemical coal cleaning method has the following characteristics:

- Coal size - 14 +28 mesh
- Temperature - ambient to 100 °C
- Pressure - atmospheric
- Efficiency - pyritic sulfur up to 100%
  - organic sulfur up to 40%
- Chemical usage - oxygen, some NO_2 and water are consumed
- Selectivity - no adverse changes in the coal
- Process time - 1 to 2 hours total

The selective oxidation is carried out on -14 +28 mesh coal at one atmosphere pressure and 100 to 200 °F. The reaction time is 0.5 to 1.0 hours. The water wash takes only a few minutes at atmospheric pressure and at 25 to 100 °C. The caustic treatment takes place from 0.5 to 1.0 hours at atmospheric pressure and at 25 - 100 °C. The total processing time is about 2 hours.

KVB's coal cleaning method differs from the ideal coal cleaning process only in the time of treatment and the degree of organic sulfur removed; however further development work could reduce these limitations.

Background information on coal cleaning methods has been reviewed by Wheelock (1977) and by Mezey, Singh and Hissong (1976) and by Meyers (1977). Because of the porous structure of coal, coarse grinding (-14 +28 mesh) is sufficient to expose the sulfur containing compounds for reaction with an oxidizing gas and subsequent washing.

Nitrogen dioxide (NO_2) has a high enough oxidation potential to oxidize inorganic and organic sulfur compounds. In the presence of oxygen, the NO formed from the NO_2 is reoxidized by oxygen. The oxidation by NO_2 and the reformation of NO_2 both take place at atmospheric pressure and low temperatures.

Oxidation Sulfur Removal

Consider the chemical reactions:

$$Fe\ S_2 + O_2 \xrightarrow{NO_2} Fe\ SO_4\ (\text{or } Fe\ SO_3) + SO_2 \qquad (1)$$

$$Fe\ S_2 + O_2 \xrightarrow{NO_2} FeO\ (Fe_2O_3) + 2SO_2 \qquad (2)$$

These chemical reactions describe the removal of sulfur from pyrites. Table 1 shows test results for four coal samples which were oxidized with oxygen, diluted with nitrogen in the presence of NO_2. All four coals showed a significant reduction in sulfur content after oxidation. No extraction or washing was employed.

The oxidations were run in a one-inch tubular reactor with a 12-inch high static coal bed. No vibration or movement of the bed of coal occurred. It is possible that under the test conditions some chanelling of gas through the bed occurred and this may account for some of the scatter of results.

In these tests total sulfur reductions of about 20 to 50 percent were observed. The reductions were about 30 to 90 percent of the pyritic sulfur content.

In these tests the oxidizing gas contained 5 to 10 percent NO_2. The total quantity of NO_2 contacting the coal at one atmospheric pressure varied from 1.0 to 2.5 moles NO_2/mole of total sulfur. The direct sulfur removal was carried out at 93 °C with about 1000 volumes of dry gas containing one volume of coal.

At the present time, it is not known for certain if the oxidation reaction with NO_2 takes place directly with the pyritic and organic sulfur or through the intermediate formation of nitric acid; for example,

$$Fe\,S_2 + 6NO_2 \longrightarrow 6NO + Fe\,SO_4 + SO_2 \qquad (3)$$

$$NO + 1/2O_2 \longrightarrow NO_2 \qquad (4)$$

Table 1. Oxidized Coal Samples.

Particle Size -14 +28 Mesh
NO_2/S Mole Ratio - 1 to 2.5 - Contacting the Coal

					% Removal	
Coal Sample	Total	Pyritic and Sulfate	Organic	Final Total Sulfur After Oxidation	of Total Initial S	of Initial Pyritic S
Lower Kitanning	4.3	3.6	0.7	3.3	23	28
Kansas Crawford Co.	6.7	5.1	1.6	4.1	24	31 29
Kansas Crawford Co.	5.3	3.8	1.5	4.3 2.7	19 49	26 68
Oklahoma Craig Co.	3.2	1.3	1.9	2.5 2.0	22 38	54 92

Possible reactions

$$H_2O + 2NO_2 + 1/2O_2 \rightleftarrows 2HNO_3 \tag{5a}$$

$$Fe\ S_2 + 6HNO_3 \rightarrow Fe\ SO_4 + SO_2 + 3H_2O + 3NO + 3NO_2 \tag{5b}$$

Water is required for the formation of nitric acid. The coal was not predried and initially may have contained 1-5 percent water. The dry gas passing over the coal would remove any water not chemically bound. The thermodynamic data for Reaction 5a (Forsythe, 1942) show that for a gas mixture of:

- 5% by volume NO_2
- 5% by volume H_2O
- 15% by volume O_2
- Balance N_2

at atmospheric pressure and 102 °C, the equilibrium concentration of nitric acid is 0.7% by volume. It is likely that this equilibrium is not achieved at the KVB process conditions. The contact of NO_2 with the coal results in selective oxidation and the formation of NO. The tests were run feeding NO and air which reacted to form NO_2. The concentration of NO_2 will be considerably less than five percent when five percent NO is fed. This would decrease the nitric acid downstream at equilibrium. The water vapor concentration assumes that for coal containing five percent water all the water is vaporized during the test. This means that no aqueous phase remains to form liquid nitric acid nor should any nitric acid formed condense as liquid nitric acid.

Any nitric acid formed which oxidized the pyrites results in the same net reaction as Reaction 3. That is, the nitric acid is generated in situ and reacts. The NO_2 would then function as indirect oxygen carrier.

Post Oxidation Water Washing to Remove Sulfur

The reaction of pyrites to sulfites or sulfates produces water soluble iron sulfur compounds. These compounds can be washed from the coal. Table 2 shows test results for coals which were oxidized and subsequently washed with water.

Table 2. Oxidized and Water Washed Coal Samples.

	Initial Sulfur Content % Of				% Removal	
Coal Sample	Total	Pyritic & Sulfate	Organic	Final Total Sulfur After Water Wash	of Total Initial S	of Initial Pyritic S
Lower Kentucky	4.3	3.6	0.7	1.6	63	75
Illinois 5	3.0	1.1	1.9	2.0	33	91
				1.9	37	100
Kansas Crawford Co.	5.3	3.8	1.5	3.0	43	61
	5.3	3.8	1.5	2.5	53	74
Moundsville (W. VA)	5.3	2.6	2.7	3.2	40	81

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Organic Sulfur Removal

Sequential oxidation and water washing reduces the sulfur content of the coal and also the iron content and the content of other trace element species. Ash removal is likely since washing coal generally reduces ash; however test verifications have not been made.

The caustic treatment is done on the partially cleaned coal to minimize the amount of caustic used up forming iron hydroxide, etc. It is also desirable to remove the iron salts before treating with caustic to avoid forming gelatinous iron hydroxides in the pores and free spaces in the coal structure as this would impede the contact of caustic with the oxidized organic sulfur compounds.

Table 3 shows the results of tests which after oxidation and water washing the coal was treated with a caustic wash for one hour at 93 °C. The final sulfur content was below the initial organic sulfur content for these samples.

To eliminate the possibility that sampling errors might have resulted in these low organic sulfur analysis results, additional tests were run using coal which was made pyrite-free by treatment with nitric acid. This treatment applied the pyritic coal analysis procedure, ASTM D2492, (i.e., the coal was boiled in 12% HNO_3 for thirty minutes, filtered and washed six times with 12% HNO_3) to a large sample of coal to prepare the sample for NO_2 oxidation. In these tests (Table 3) the sulfur content was reduced indicating that the organic sulfur was indeed being removed from the coal.

Organic Sulfur Removal Chemistry

Using NO_2 as an oxygen carrier for the selective oxidation of sulfur compounds in coal provides a strong oxidant and permits the reactions to be carried out at ambient conditions. It is possible to oxidize the sulfur compounds selectively. It is also possible

Table 3. Oxidized Water Washed and Caustic Washed Coal Samples.

Coal Sample	Initial Sulfur Content				% Removal	
	Total	& Pyrite Sulfate	Organic	Final Sulfur	of Total Sulfur	of Organic Sulfur
Lower Kittaning	4.3	3.6	0.7	0.5	88	29
Illinois 5	3.0	1.1	1.9	1.0	67	47
	3.0	1.1	1.9	1.2	60	37
Moundsville (W. VA)*	2.8	--	2.8	1.6†	43	43

* Sample was pretreated to remove pyrites. Initially this sample analyzed 5.3% total sulfur, 2.6% pyritic (and sulfates) 3.2% organic

† After oxidation and caustic treatment

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to cause non-selective reactions to occur. Depending on the temperature, pressure and concentration, NO_2 can:

- react selectively to oxidize sulfur compounds
- react with coal to form easily decomposed nitrogen-containing compounds
- react with coal to form stable nitrogen-containing compounds
- react to oxidize coal

The pyrite oxidation reactions were discussed above. Suffice it to say that if inorganic nitrates are formed along with inorganic sulfates, they are water soluble. The selective oxidation of organic sulfur compounds is widely in the literature. KVB has patented a process using oxygen containing gases containing low quantities of nitrogen oxides to oxidize the sulfur compounds in petroleum fractions and subsequently separate the oxidized sulfur compounds by methanol extraction (Guth, 1974). Typical results for desulfurizing fuel oils are given in Table 4. In these tests the oil was oxidized at atmospheric pressure and 25 to 65 °C. The oxidized oil was allowed to degas for one hour. The oil insoluble fraction separated and was further degased after 10 minutes at 150 °C. The oxidized degassed oil was extracted with methanol to separate to low sulfur fraction as the raffinate and the high sulfur oil as the extract.

These data are presented to indicate that the various types of organic sulfur compounds in oil fractions can be oxidized with NO_2 in the presence of oxygen without forming stable nitrogen containing compounds. Nitrogen compounds along with sulfur compounds are oxidized and extracted. Methanol extraction of unoxidized oil does not separate any significant fractions of the sulfur and nitrogen.

Model sulfur compounds have been oxidized to sulfones and sulfoxides by NO_2 in the presence of air. Typical of the compounds are dihexyldisulfide, benzylphenylsulfide and dibenzyldisulfide by KVB and dibenzothiophene by the Bureau of Mines (Friedman, 1977). Both aliphatic and aromatic sulfur compounds are oxidized without nitration.

Coal oxidation may be accompanied by nitrogen dioxide absorption under some conditions. It may be necessary to predry the coal to eliminate a water phase or to post heat the coal to decompose unstable nitrogen compounds to reduce the abosrbed NO_2 content.

Table 4. Organic Sulfur Compound Oxidation in Petroleum Fractions.

	Initial		Low Sulfur			High Sulfur			Oil Insoluble		
Feed	%S	%N	% Of Feed	%S	%N*	% Of Feed	%S	%N*	% Of Feed	%S	%N†
Turbine fuel APIG	0.15	0.03	85	0.06	0.01	14.5	0.66	0.26	0.5	0.3	0.5
Diesel oil APIG 34	1.1	0.19	85	0.1	0.08	14	7.0	0.8	1.0	5.0	0.5
Atmospheric gas oil APIG 28	1.7	0.25	80	0.3	0.12	19	7.5	0.8	1.0	5.0	0.5
Shale oil APIG 30	0.6	1.6	85	0.4	0.3	14	1.7	9.0	1.0	0.8	1.5

* After degassing one hour at 30 °C

† After degassing 10 minutes at 150 °C

In coal desulfurization to remove organic sulfur, it is not possible selectively to dissolve and separate the oxidized sulfur compounds; however, the oxidized sulfur compounds can be hydrolyzed. The caustic treatment hydrolyzes the oxidized organic sulfur compounds in coal converting the sulfur to inorganic forms thereby allowing the sulfur to be spearated by extractions.

The question of NO_2 reacting nonselectively with coal has not been answered. More laboratory work is required. If NO_2 reacts with coal in a manner similar to the reactions with oils, any NO_2 reacting with the coal will be readily removed by heating and the NO recovered for reuse. If NO_2 reacts with coal to form more stable compounds, then reaction conditions must be used to minimize the nonselective NO_2 reaction and thereby minimize any contribution to flue gas NOx on combustion of the coal.

Process Cost Estimate

KVB's process has the following operations:

- Preparation of the feed - white rock removed and coal crushed to -14 +28 mesh size
- Oxidation - the dry crushed coal is reacted at one atmosphere and 100 °C with a gas stream containing nitrogen dioxide and oxygen
- Water washing - the oxidized pyritic sulfur is removed fromthe coal by a water wash at one atmosphere pressure and 100 °C
- Caustic washing - about 40% of the organic sulfur is removed by a caustic washing at one atmosphere pressure and 100 °C

- Pelletizing - about 30% to 35% of the feed coal is less than 28 mesh size and is balled on a disc and dried on a traveling grate prior to shipment. The remainder of the coal can be shipped as-is.
- Wash solvent treating - the process wastes, calcium sulfate and sodium jerosite (sodium, iron, sulfate compound) are chemically separated from the water solvents

There are at this time uncertainties regarding the chemical usage and process equipment requirements. However, KVB has made a preliminary R.O.M. cost estimate.

KVB used the Bechtel study comparing chemical coal cleaning processes (Oder, 1977) as a basis for an updated cost estimate. The Bechtel study showed that KVB was comparable in cost to other processes under consideration. Cost reduction in KVB's analysis resulted mainly using a coarser grind coal. The KVB estimate was made of the cost of operating an 8,000 ton/day coal treatment plant based on the schematic shown in Figure 2. The major cost reductions were in coal grinding, compaction and energy to dry coal in the processes. The capital cost estimate was arrived at by estimating equipment costs and applying a factor to obtain installed equipment costs. The factor of 4 used by KVB is believed to be conservative. A 30% contingency was added due to the uncertainty of the estimate. The capital cost was estimated to be $29,000,000 as shown in Table 5, and the total cost per ton of feed was $8.50 as shown in Table 6. Both the capital cost and the operating cost are R.O.M. estimates based on the current understanding of the process.

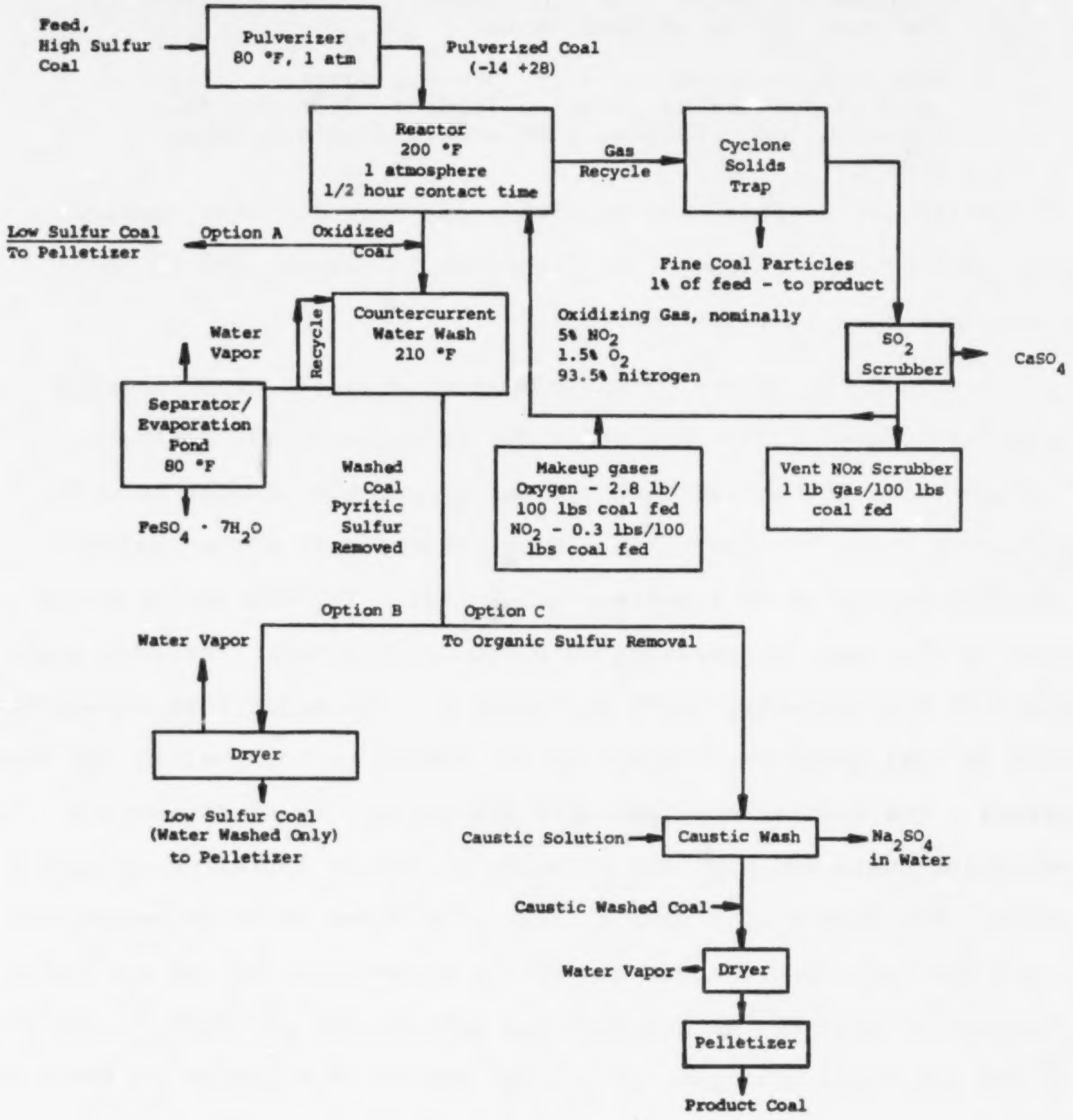
Feed, High Sulfur Coal
Pulverizer 80 °F, 1 atm
Pulverized Coal (-14 +28)
Reactor 200 °F 1 atmosphere 1/2 hour contact time
Gas Recycle
Cyclone Solids Trap
Low Sulfur Coal To Pelletizer
Option A
Oxidized Coal
Fine Coal Particles 1% of feed - to product
Countercurrent Water Wash 210 °F
Recycle
Water Vapor
Oxidizing Gas, nominally 5% NO2 1.5% O2 93.5% nitrogen
SO2 Scrubber
CaSO4
Separator/ Evaporation Pond 80 °F
FeSO4 · 7H2O
Washed Coal Pyritic Sulfur Removed
Makeup gases Oxygen - 2.8 lb/100 lbs coal fed NO2 - 0.3 lbs/100 lbs coal fed
Vent NOx Scrubber 1 lb gas/100 lbs coal fed
Option B
Option C
Water Vapor
To Organic Sulfur Removal
Dryer
Low Sulfur Coal (Water Washed Only) to Pelletizer
Caustic Solution
Caustic Wash
Na2SO4 in Water
Caustic Washed Coal
Water Vapor
Dryer
Pelletizer
Product Coal

Figure 2. Process Flow Sheet.

Table 5. Capital Cost Estimate for KVB Coal Desulfurization Process for 8,000 ton/day Feed (Lump Coal)

	Equipment	MM$
1.	Feed storage and handling, grinding and product pelletizing	1.30
2.	Reactor and oxidizing gas loop	1.3
3.	Water wash use and reclaiming	0.7
4.	Caustic use and reclaiming	0.7
5.	Dryer for coal	0.75
6.	Solids preparation for disposal	0.10
	Total Equipment	4.85
	X Factor for Installed Equipment (X4)	19.4
	Contractor's Fee	2.9
		22.3
	Contingency at 30%	6.7
	Total Capital Cost	29.0

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Table 6. Processing Cost Estimate for KVB Coal Desulfurization Process

Feed Rate - 8,000 Tons/Day, 330 days, 2.6 MM Tons/Year

Capital Investment, Million $	29.0
Operating Costs	MM$/Yr
Direct Costs	
NO_2 at $200/ton	1.6
Oxygen at $30/ton	2.1
Caustic at $300/ton	1.9
Lime at $30/ton	0.1
Utilities (energy, water)	7.0
Labor (5 men/shift)	0.5
Maintenance, 5% of capital	1.4
Total Direct	14.6
Indirect Costs	
Taxes and insurance (1.8% capital); supervision (2.0% of labor); benefits (30% of labor plus supervision); plant overhead (50% of labor plus supervision)	
Total Indirect	1.0
Corporate G&A (10% of direct cost plus indirect)	1.5
Total Operating Cost	17.1
Amortization, 0.17 x capital (15% ROI, 15-year life, 52% income tax rate)	4.9
Total Expense	22.0
TOTAL COST/TON OF FEED*	$8.50

*Feed Coal:	Product Coal:
Sulfur, 1.9%	Sulfur, 0.5%
Pyritic, 1.2%	
Organic, 0.7%	

KVB feels that the estimated processing cost of $8 to $9/ton is representative of the process as is known today.

The costs of the operations are roughly as follows:

Storage, grinding, pelletizing	1.50
Oxidation	3.00
Water wash	1.50
Caustic wash	2.50
	8.50/ton

Operating with only one or two of the desulfurization modes of KVB's process would result in lower costs.

Oxidation only of previously ground coal is estimated to cost $3.00-$4.00/ton.

Oxidation and caustic washing for organic sulfur removal of a low pyrite coal is estimated to cost about $6.00 to $7.00/ton.

REMARKS

The United States' largest energy resource is coal. The ability efficiently to utilize this source of energy is vital to the nation's technological progress, economic well-being, and, perhaps, national defense. This is highlighted by our well-publicized dependence on imported oil. Unfortunately, the use of coal as a fuel is less desirable from an environmental standpoint than gas or oil. Emissions of sulfur oxides, nitrogen oxides, and particulate matter are more difficult to control.

The KVB process has the potential of an economic chemical coal cleaning process. It is an atmospheric pressure, ambient temperature process which results in low capital cost. The feed does not have to be pulverized (+28 mesh has typically been used). The chemicals used are oxygen and nitrogen dioxide which are relatively low cost. Of particular importance is the removal of a portion of the organic sulfur content in addition to essentially all pyritic sulfur. Washing of coal to remove pyrites by physical separation is feasible but requires pulverized coal (as fine as 200 mesh), results in incomplete separation, and removes no organic sulfur. Substantial reductions in the cost of scrubbing can be achieved by using cleaned coal.

KVB has demonstrated the technical feasibility of the process for removal of sulfur from several coal samples. Preliminary estimates have been made of the cost of treating coal and they compared favorably with competing processes. Additional experimental work must be done to further the process development and provide a basis for a laboratory plant design (about 100 lb/day capacity). Questions regarding NO_2 uptake by the coal and the application to coals previously physically cleaned to remove pyrites must be answered.

This presentation described three sulfur removal modes associated with KVB's chemical coal cleaning method:

- gas phase - on oxidation
- water phase - washing the oxidized coal
- caustic phase - treating the water washed oxidized coal for organic sulfur removal

The test data are not extensive or complete; however, they do indicate that the chemical basis of this technology is sound.

Further development will be aimed at expanding the data base, refining the cost estimate and lowering the cost. Applications to coals previously cleaned by physical methods will be investigated.

This method can be a practical means for low cost chemical coal cleaning.

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THE DRY REMOVAL OF PYRITE AND ASH FROM COAL BY THE MAGNEX PROCESS COAL PROPERTIES AND PROCESS VARIABLES

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ABSTRACT

The Magnex process is a dry method for removing pyrite and other ash-forming minerals (ash) from coal. The process works because of the action of a chemical vapor which increases the magnetic susceptibilities of pyrite and ash but not the associated coal. As a result, pyrite and ash can be removed from coal by conventional magnetic separators.

Conventional coal cleaning processes are limited (dependent upon) the specific gravity distribution of the coal which, in turn, is dependent upon the naturally occurring, sometimes intimate, mixtures of coal, ash, and pyrite. In like manner, high gradient magnetic separators are limited by fixed magnetic susceptibilities of the component assemblages. In contrast, Magnex, an applied chemical process, permits the adjustment of the magnetic susceptibility of refuse components independent of the coal and independent of the way nature assembled them.

Recent detailed studies of the Magnex process variables and coal properties are permitting us to take advantage of the selectivity of the process. In this regard, six coals are discussed. The effects of pretreatment and carbonyl treatment variables on pyrite and ash removal efficiencies illustrate the range of control that is possible over the magnetic susceptibility enhancement reactions. Also, examples are given of the "best path" approach which leads to clean coal results equivalent to perfect gravity cleaning. Future plans for Magnex are discussed.

INTRODUCTION

There exists today, a time of importance in achieving both energy and environmental goals, a great need for an efficient and inexpensive process for removing pyrite and ash from fine coal. The Magnex process, a novel method for fine coal cleaning, is a candidate to fulfill that need. This paper reviews the current status of the process and its commercialization. Also, it describes current progress in a study undertaken with several coals to acquire a better understanding of the interaction between properties of the feed coal and the process, and the relationship between the process variables and effective coal cleaning.

Nedlog Technology Group, Arvada, Colorado, holds the worldwide licensing rights to the Magnex process, and they are sponsoring the research and development work at Hazen Research, Inc. Grateful acknowledgment is extended to them for their sponsorship and this opportunity to review some aspects of the work.

PROCESS REVIEW

There are four main steps in the Magnex process:

1. CRUSHING: To achieve liberation of pyrite and ash forming minerals (ash); it usually is necessary to comminute to about 14-mesh.

2. HEATING: In this step the temperature of the feed coal is elevated to about 170°C. In addition to being a heating step, preconditioning takes place which makes the carbonyl treatment more selective.

3. CARBONYL TREATMENT: The iron carbonyl treatment provides the magnetic enhancement of the pyrite and the ash-forming minerals.

4. MAGNETIC SEPARATION: Pyrite and ash-forming minerals are removed by medium intensity magnets as a magnetic refuse while the nonmagnetic portion is a clean dry coal.

The chemistry of the Magnex process is summarized with three equations:

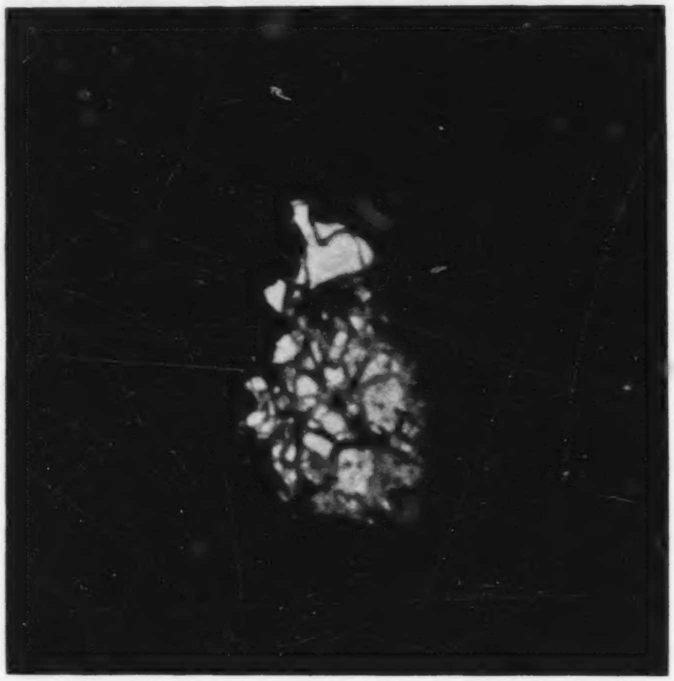
$$\underset{\substack{\text{Iron}\\\text{pentacarbonyl}}}{Fe(CO)_5} \rightleftharpoons \underset{\text{Iron}}{Fe^{o}} + \underset{\substack{\text{Carbon}\\\text{monoxide}}}{5CO}$$

$$\underset{\substack{\text{Iron}\\\text{pentacarbonyl}}}{Fe(CO)_5} + \underset{\text{minerals}}{\text{Ash}} \rightarrow \underset{\substack{\text{Crystallites of}\\\text{iron on ash}\\\text{minerals}}}{Fe^{o}\cdot\text{Ash}} + \underset{\substack{\text{Carbon}\\\text{monoxide}}}{5CO}$$

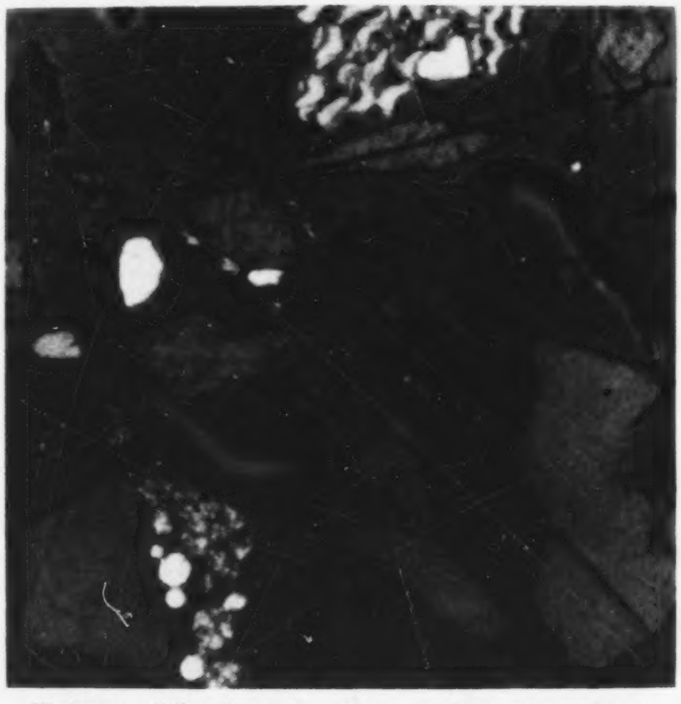
$$\underset{\substack{\text{Iron}\\\text{pentacarbonyl}}}{(1-2x)\ Fe(CO)_5} + \underset{\text{pyrite}}{FeS_2} \rightarrow \underset{\substack{\text{Pyrrhotite-like}\\\text{material}}}{2Fe_{1-x}S} + \underset{\substack{\text{Carbon}\\\text{monoxide}}}{(5-10x)CO}$$

The first equation symbolizes the thermal breakdown of iron pentacarbonyl into iron and carbon monoxide. This is reported to occur at temperatures greater than 110°C. The kinetics of this reaction have been studied. (Carlton and Oxley, 1965). At process temperatures (below 200°C), surface kinetics of adsorbed iron carbonyl are primarily rate limiting. The second equation describes how the ash-forming minerals become magnetic. Here, iron pentacarbonyl decomposes at the ash surface to form crystallites of iron on the ash and release carbon monoxide. The third equation describes what happens to the pyrite. It reacts with iron pentacarbonyl to form a pyrrhotite-like material and carbon monoxide. The iron carbonyl does not react with the coal to form a magnetic species under selected operating conditions. After treatment, there are ferromagnetic iron crystallites on the ash, and on the surface of pyrite a pyrrhotite-like conversion which has a quite large magnetic susceptibility. Both can easily be removed by magnetic separators. In summary, the process works because iron carbonyl selectively decomposes on the ash and reacts with pyrite but will not produce any significant deposit of iron on the surface of the coal.

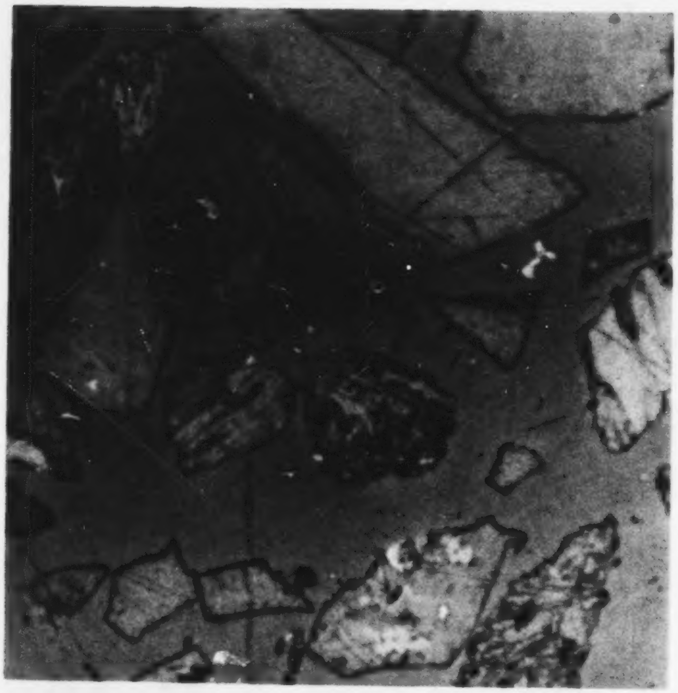
Figure 1 is a photomicrograph of a piece of pyrite which was carbonyl treated. This particle is about 65-mesh, and the formation of the pyrrhotite-like material can be seen on periphery and in the cracks, the lighter, brighter material being the original unconverted pyrite. Only a slight conversion of pyrite to pyrrhotite-like material or only a slight deposition of iron on the ash is required to permit the particles to be magnetically drawn into the refuse. Photomicrographs of a feed coal, clean coal, and refuse from a typical Magnex separation are shown in Figures 2, 3, and 4.



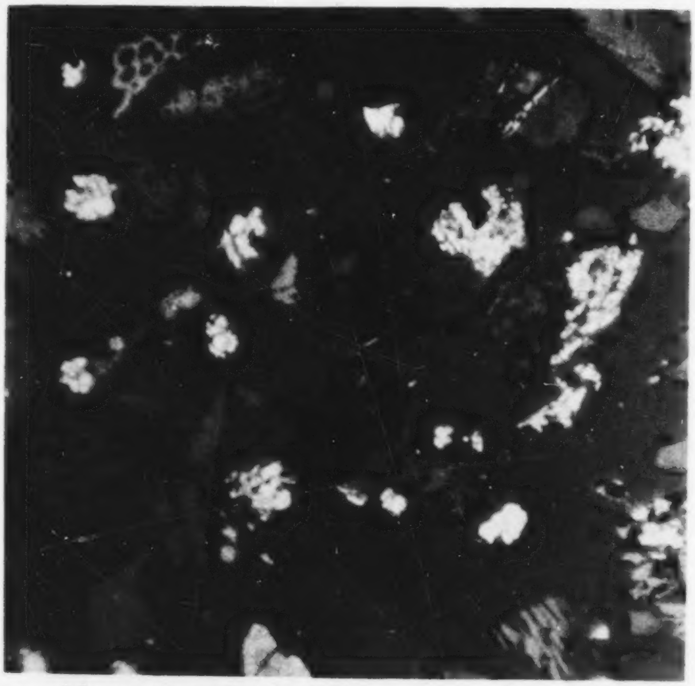
Photomicrograph of pyrite after treatment with iron carbonyl 275X
Figure 1



Untreated feed coal. Minus 65-mesh 200X
Figure 2



Nonmagnetic clean coal. Minus 65-mesh 200X
Figure 3



Magnetic refuse. Minus 65-mesh 90X
Figure 4

The Magnex process was invented at Hazen Research in 1975. Since that time there have been numerous bench scale studies of the process. Magnex processing involves pretreatment and carbonyl treatment of crushed coal. The pretreatment and carbonyl treatment are done in a rotating glass reactor; the magnetic separations are made on a laboratory crossbelt separator. In addition to the supporting analytical work, other tests were performed to determine the process mechanisms and to improve the selectivity.

Based upon the successful laboratory development program and a favorable economic study, a 200 lb/hr pilot plant was designed and constructed to test the process on a continuous basis. A feed coal for the pilot plant was obtained from the Allegheny Group coals and crushed to 14-mesh. The coal was pretreated, iron carbonyl treated, and magnetically separated; crushing and magnetic separation were not continous with pretreatment and carbonyl treatment. Crushing was accomplished with a jaw and impactor crushers. Indirect heating, and pretreatment with steam at atmospheric pressure were done while the coal passed through a screw conveyor. Carbonyl treatment was accomplished in a shaft furnace with a very slow co-current flow of iron carbonyl gas, also at atmospheric pressure. Magnetic separation was completed with a commercially available induced magnetic roll separator. These pieces of equipment were a convenience for pilot plant operation and are not necessarily the ones which would be used in a larger installation.

The pilot plant was operated continuously during five campaigns; each campaign lasted from four to six days. Coal processed continuously through the pilot plant behaved as expected from laboratory tests on the same coal. Samples from the pilot plant operation met the EPA limits for SO_2 emissions from new sources, 1.2 pounds/million Btu. Data showing the quality of clean coal in comparison to feed coal are given in Table 1.

Table 1

Comparison of Feed and Clean Coal:
Pilot Plant Results

	Yield Weight %	Ash, %	Pyritic Sulfur, %	Total Sulfur, %	Calorific Value, Btu/lb	Pounds of Sulfur/ MM Btu
Clean coal	82.3	14.8	0.07	0.73	12,520	1.17
Feed coal	100.0	18.1	0.62	1.22	11,981	2.03

An economic study based upon data obtained from the pilot plant showed that the operating cost was about equal to the cost of cleaning fine coal in existing coal preparation circuits.

Current plans and activities include:

1. Intensive studies on iron carbonyl generation. This work has been most successful and is now in the pilot plant stage.
2. Intensive search for alternate magnetic separators to separate large volumes of dry solids efficiently and inexpensively. This work is just under way.
3. Operate the pilot plant again, but with the coal selected for the demonstration plant. Provide support for the design engineers.
4. Design a coal preparation flowsheet which employs the best blend of the advantages of conventional coal processing and the Magnex technology.

5. Improve the scope and efficiency of the process and reduce the cost.

6. Proceed to a demonstration plant, about 60 TPH.

This completes the process review and status; following are two studies or evaluations dealing with the effect of the coal properties on Magnex beneficiation, and the relationship between process variables and Magnex beneficiation.

EFFECT OF COAL PROPERTIES ON MAGNEX BENEFICIATION OF COAL

When cleaning coal of a given size range with any gravity separator (jig, table, heavy media, etc.), it is the specific gravity of the coal, ash, and pyrite particles, whether free or locked, which determine the kind of separation obtained. This specific gravity distribution is not subject to human control. Likewise, a magnetic (HGMS) separation of raw coal (no Magnex treatment) is dependent upon the relative naturally occurring magnetic susceptibility of the various particles and also is not subject to human control. In contrast, the Magnex process permits the controlled enhancement of the magnetic susceptibility of particles containing ash or pyrite while not affecting particles of clean coal. This selectivity, the ability to enhance magnetic susceptibility of refuse but not coal, is the great opportunity and challenge of the Magnex process.

COAL CHARACTERISTICS

During the development of the Magnex process, numerous coals were tested for their amenability to the process. These tests were done in the laboratory on a batch basis; however, many results have shown the good agreement between laboratory and pilot plant results. Coals from several localities were tested. These coals differed considerably in their responsiveness to carbonyl treatment and were included in this study for that reason. Of course, differences should be expected because of the highly variable nature of coal and associated minerals.

An intensive study was mounted on seven coals which varied in their response to the process. The purpose of the study, which is still in progress, is to learn which properties of coal influence the process and to determine how process variables could be changed to bring about improved results. The coals considered are listed in Table 2.

Table 2

Identification of Coal Samples

HRI Number	Seam	State
11986-1	Lower Freeport No. 6A	Ohio
12683	Pittsburgh No. 8	West Virginia
11986-2	Pittsburgh No. 8	Ohio
11089	Allegheny Group Coals	Pennsylvania
7265	Illinois No. 6	Illinois
6776-1	Lower Freeport	Pennsylvania
6145	Lower Freeport	Pennsylvania

Each of these coals was tested for those coal properties which were thought might be related to its response to the process. A listing of these coal properties is given in Table 3. The last five analyses included in the list are tests which are not ordinarily determined in coal. They are included because study and correlation of the previous test work has suggested a relation between them and the process.

Table 3

Feed Coal Properties

- Ash
- Pyritic sulfur
- Organic sulfur
- Total sulfur
- Calorific value
- Sink float tests

- Low temperature volatiles
- Tendency to produce acid
- Heavy metal analysis
- Pyrite size
- Elemental sulfur

BENEFICIATION TESTS BY THE MAGNEX PROCESS

Each of the seven coals was then beneficiated by the Magnex process. This involved crushing, and magnetically separating the treated material to produce a clean coal and refuse. The clean coal, refuse, and feed were then analyzed for ash, forms of sulfur, and calorific value (Btu/lb). These data and other analyses performed on the feed coal appear in Table 4.

Table 4

Analyses of Feed, Clean Coal, and Refuse for Seven Minus 14-mesh Coals Beneficiated by the Magnex Process

Sample Identification		Yield, Weight %		Pyritic Sulfur, %	Organic Sulfur, %	Total Sulfur, %	Calorific Value, Btu/lb	Rejection			Btu Recovery, %	Sulfur Oxides, Pounds/10^6 Btu	1/ Btu/SO_2 Index(B_I)	2/ Percent Theor. Cleaning	Percent of Perfect Gravity Cleaning		Low 4/ Temperature Volatiles Arbitrary Units	Net 5/ Acid Production % $SO_4^=$	Metal Analysis		Weight Mean Pyrite Diameter Micron
								Ash, %	Pyritic Sulfur, %	Total Sulfur, %					Ash	Pyritic Sulfur			Zinc, ppm	Copper, ppm	
Lower Freeport No. 6A	Clean coal	74.5	18.4	0.69	0.70	1.39	11,953	-	-	-	95.5	2.32	41.2	47	68	221	-	-	-	-	-
Ohio	Refuse	25.5	76.8	7.08		6.97	2,326	53.8	77.8	63.2	-	-	-	-	-	-	-	-	-	-	-
HRI 11986-1	Feed		34.3	2.32	0.66	2.98	9,320	-	-	-	-	6.39	15.6	-	-	-	92.0	0.63	100	5	556
Pittsburgh No. 8	Clean coal	83.7	21.0	1.24	2.34	3.58	11,605	-	-	-	92.5	6.16	15.0	27	52	272	-	-	-	-	-
West Virginia	Refuse	16.3	60.7	9.46		8.89	4,037	36.0	59.8	32.6	-	-	-	-	-	--	-	-	-	-	-
HRI 12683	Feed		27.5	2.38	2.26	4.64	10,505	-	-	-	-	5.82	11.3	-	-	-	303.6	0.194			619
Pittsburgh No. 8	Clean coal	84.4	26.0	1.52	1.63	3.15	10,644	-	-	-	95.2	5.92	16.1	22	49	157	-	-	-	-	-
Ohio	Refuse	15.6	61.0	10.8		11.3	3,446	32.9	56.9	39.9	-	-	-	-	-	-	-	-	-	-	-
HRI 11986-2	Feed		33.3	2.76	1.36	4.32	9,433	-	-	-	-	9.15	10.9	-	-	-	116.5	0.330	53	17	405
Allegheny Group Coals	Clean coal	86.6	16.3	0.07	0.65	0.72	12,178	-	-	-	90.8	1.18	76.9	75	~37	117	-	-	-	-	-
Pennsylvania	Refuse	13.4	38.5	4.32	-	4.24	3,517	26.8	90.5	47.7	-	-	-	-	-	-	-	-	-	-	-
HRI 11039	Feed		19.7	0.64	0.66	1.30	11,616	-	-	-	-	2.24	44.6	-	-	-	12.7	0.182	140	13	419
Illinois No. 6	Clean coal	79.4	12.9	0.94	3.34	4.28	11,891	-	-	-	94.6	7.19	13.2	48	76	72	-	-	-	-	-
Illinois	Refuse	20.6	59.6	5.45	-	5.69	4,818	54.5	60.0	25.6	-	-	-	-	-	-	-	-	-	-	-
HRI 7265	Feed		25.5	1.87	3.01	4.33	9,977	-	-	-	-	9.77	10.2	-	-	-	88.0	0.59	90	53	641
Lower Freeport	Clean coal	89.2	23.9	0.57	0.51	1.08	11,419	-	-	-	95.1	1.89	50.4	48	40	136	-	-	-	-	-
Pennsylvania	Refuse	10.8	62.9	11.2		13.0	4,498	24.2	70.3	59.3	-	-	-	-	-	-	-	-	-	-	-
HRI 6776-1	Feed		27.9	1.72	0.66	2.38	10,707	-	-	-	-	4.44	22.5	-	-	-	19.0	-	81	17	-
Lower Freeport	Clean coal	72.7	9.4	0.33	0.55	0.88	13,970	-	-	-	88.3	1.26	70.2	63	-	-	-	-	-	-	-
Pennsylvania	Refuse	27.3	73.8	6.19		7.28	2,980	74.7	87.6	75.7	-	-	-	-	-	-	-	-	-	-	-
HRI 6145	Feed		25.7	1.93	0.58	2.51	11,504	-	-	-	-	4.36	22.9	-	-	-	9.5	-	48	17	513

1/ Btu/SO_2 Index (B_I) = $\frac{\text{Btu recovery}}{\text{Sulfur-to-Btu ratio}}$

2/ Percent theoretical cleaning (PTC) = $\frac{B_I \text{ feed} - B_I \text{ clean coal}}{B_I \text{ feed} - B_I \text{ theoretical}} \times 100$

B_I theoretical assumes complete pyrite and ash removal but no Btu loss from organic material.

3/ Percent of perfect gravity cleaning, the ratio of ash or pyritic sulfur removed by the process to the ash or pyritic sulfur removed by sink-float at the same yield times 100.

4/ Low temperature volatiles, quantity of gas given off by heating the coal to 200°C for five minutes. Expressed in arbitrary units.

5/ Net acid production, amount of acid found by sparging oxygen through a coal-water slurry at 75°C for 24 hours less the amount of acid resulting from sparging with nitrogen. Expressed in percent $SO_4^=$.

To judge the effectiveness of the separations, several criteria derived from the analytical data are useful. For steam coals, it is desirable to maximize Btu recovery and minimize the sulfur-to-Btu ratio; for this reason "Btu recovery" and "pounds of sulfur oxides per million Btu" are calculated. Btu/SO_2 Index (B_I) is a combination of Btu recovery and sulfur-to-Btu ratio; it is defined as follows:

$$\text{Btu/SO}_2\text{ Index }(B_I) = \frac{\text{Btu Recovery}}{\text{Sulfur-to-Btu Ratio}}$$

The B_I value for the feed coal is 100% Btu recovery divided by the pounds of SO_2 per million Btu contained in the feed. Clean coal has lower Btu recovery but also lower SO_2 values. High B_I values are desirable, reflecting good Btu recovery and low sulfur-to-Btu ratio.

For comparisons between coals, the B_I value is used to develop the percent of theoretical cleaning (PTC). It is calculated as follows:

$$\text{PTC} = \frac{B_I\text{ feed} - B_I\text{ clean coal}}{B_I\text{ feed} - B_I\text{ theoretical}}$$

B_I theoretical is the calculated value for complete ash and pyrite removal with no loss of Btu from loss of organic material.

In addition to the above, an efficiency measure is needed which considers the cleaning achieved relative to that theoretically attainable by sink-float methods. The ash error (difference in sink-float and clean coal ash at the same yield) and the Frasier-Yancy or organic efficiency (relationship of yield of clean coal relative to yield of sink-float coal at the same ash value) are two such measures. A similar criterion used in this work is the "Percent of Perfect Gravity Cleaning;" it is the ratio of ash or pyritic sulfur removed by the process to the ash or pyritic sulfur which is removed by sink-float at the same yield.

CORRELATION STUDY

Having described some of the criteria for judging the effectiveness of the separation, the data of Table 4 can be reviewed for trends. A complete correlation study was made on all of the data by developing the simple correlation coefficients for each data pair. Selected correlations are shown in Table 5. The significance and utility of the correlations for understanding and controlling the process are now being evaluated. The correlation study supports the following statement. A high quality Magnex separation is associated with the following properties of the feed coal:

1. Small amount of low temperature volatiles.
2. A tendency to produce acid.
3. Lower levels of copper and perhaps higher levels of zinc.
4. Lower pyrite and organic sulfur content.

This information, and other information expected when the correlation study is completed can be used to improve the process, to characterize feed coals, or to lead to an understanding of the process mechanism.

Table 5

Correlation of Feed Coal Properties with the Results of Magnex Cleaning

(Numbers are the simple correlation coefficients, r)

Low Temperature Volatiles in the Feed Coal (7 Coals Correlated, r >0.6

0.71+	Pyritic sulfur in the clean coal
0.67+	Total sulfur in the clean coal
0.69+	Pounds of SO_2/MM Btu in the clean coal
0.65-	Pyrite rejection
0.74-	Percent theoretical cleaning [2]

Net Acid Production of the Feed Coal [3] (5 Coals Correlated, r >0.5

0.84+	Organic sulfur in the clean coal
0.75+	Total sulfur in the clean coal
0.74+	Pounds of SO_2/MM Btu in the clean coal
0.56-	Pyrite rejection
0.82-	Total sulfur rejection

Zinc in Feed Coal (6 Coals Correlated, r >0.5

0.54-	Pyritic sulfur in the clean coal
0.75-	Ash in the refuse
0.55-	Pyritic sulfur in the refuse
0.58-	Total sulfur in the refuse
0.75+	Btu in the refuse
0.58+	Percent theoretical cleaning

Copper in Feed Coal (6 Coals Correlated, r >0.5)

0.91+	Organic sulfur in the clean coal
0.79+	Total sulfur in the clean coal
0.74+	Pounds of SO_2/MM Btu in the clean coal
0.53-	Pyritic sulfur rejection
0.71-	Total sulfur rejection

Pyritic Sulfur in the Feed Coal (7 Coals Correlated, r >0.6)

0.88+	Pyritic sulfur in the clean coal
0.74+	Ash in the refuse
0.65+	Pyritic sulfur in the refuse
0.82-	Btu in the refuse
0.71-	Btu rejection
0.91-	Percent theoretical cleaning

Organic Sulfur in the Feed Coal (7 Coals Correlated, r > 0.6

0.73-	Pyritic sulfur rejection
0.87-	Total sulfur rejection

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[1] Low temperature volatiles, quantity of gas driven off of the coal at 200°C in five minutes.

[2] Net acid production, amount of acid formed by oxygen sparging a coal-water slurry at 75°C for 24 hours less the amount of acid resulting from sparging with nitrogen.

[3] Percent of theoretical cleaning is the difference between the ratio of Btu recovery to pounds of SO_2 per million Btu in the feed minus that ratio in the clean coal, divided by the difference between that ratio in the feed and that ratio in a theoretically perfectly cleaned coal, complete recovery of organic Btu and complete rejection of pyrite and ash. See text, page 13.

For the Magnex test on the Lower Freeport No. 6A coal (HRI 11986-1), 221% more pyritic sulfur was removed than could have been removed by perfect gravity cleaning at the same coal yield; however, only 68% as much ash was removed as could have been removed by sink-float. This shows the extreme selectivity of the Magnex process for removing pyrite. Greater than 100% of perfect gravity cleaning is possible because the Magnex process cleans coal on the basis of the magnetic susceptibility of the refuse rather than its specific gravity. For example, a locked coal-pyrite grain which floats could be pulled into the refuse by the Magnex process or a piece of bony coal which sinks might be left in the Magnex clean coal.

THE RELATIONSHIP BETWEEN PROCESS VARIABLES AND MAGNEX BENEFICIATION

In each of the four steps of the Magnex process there are several controlling variables. A listing of some of these is given in Table 6. The study of these variables is by no means complete; in fact, for some of the steps (crushing and magnetic separation) it has just begun.

PYRITE SIZE DISTRIBUTION

Most of the development work on this process used coal crushed to 14-mesh. This size was chosen because it gave substantial liberation of pyrite as judged from examination of polished sections. An objective measure of pyrite size distribution was desired to determine if there was a correlation between pyrite particle size and pyrite removal.

Table 6

Selected Process Variables

Crushing:
- Top size
- Size consist

Pretreatment:
- Time
- Temperature
- Atmosphere (steam)

Iron carbonyl treatment:
- Time
- Temperature
- Iron carbonyl concentration
- Cotreatment with other gases

Magnetic separation:
- Type of separator
- Field strength
- Gradient

The size determination was made by examining numerous polished sections of coal. For each coal, 1,500 pyrite grains larger than 5 microns were measured. The measurements were carried out by subjecting the high optical quality polished sections to automatic image analysis. The analysis used a television scanner connected to a microscope. Based on its reflectivity,only pyrite grains were measured, and measurements, area and shape, were processed by a Quantimet 720 image analysis computer. The weight distribution was calculated from an area measurement of each grain.

Table 7 shows the weight mean diameter of pyrite (50% by weight of the pyrite has smaller, or larger, diameters) and the frequency mean diameter of pyrite (50% of the grains have smaller, or larger diameters). Additionally, the table shows the weight distribution of coal between 5, 25, 50 microns, and greater. Considering the small percentages of pyrite in the ranges 5-25, 25-50, and 50-100 microns and the mean pyrite size, which ranges from about 490 to 640 microns, removal of the coarse pyrite becomes extremely important. Regarding the finest pyrite grains, even if none of these were removed, they would make only a minor contribution to the sulfur content of the clean coal.

CARBONYL TREATMENT

For the carbonyl treatment, the variables time, temperature, and amount of iron carbonyl have to be fixed such that the desired result is obtained. Also, the carbonyl treatment can be applied to a coal which either has or has not been pretreated. A half-replicate 2^4 factorial experiment was conducted with the Lower Freeport No. 6A, Ohio, HRI 11986-1, coal to test the effect of pretreatment and the three named variables. (A portion of this work was sponsored by the Ohio Department of Energy, Grant No. 77-10).

The amount and quality of the clean coal provided the bases for judging the effectiveness of the separation. Specifically, the responses evaluated for the clean coal were:

Measured responses:
- Yield
- Ash
- Pyritic sulfur
- Calorific value

Table 7

Data on the Size Analysis of Pyrite in Coal
(Coal crushed to minus 14-mesh)

HRI Number	Coal Identification		Weight 1/ Mean Diameter of Pyrite, Micron	Frequency 2/ Mean Diameter of Pyrite, Micron	Size Distribution in Percent Weight Basis			
	Seam	State			5-25 Micron	25-50 Micron	50-100 Micron	>100 Micron
11986-1	Lower Freeport No. 6A	Ohio	556	21	0.3	0.8	2.0	96.9
12683	Pittsburgh No. 8	West Virginia	619	16	0.3	0.8	1.4	97.5
11966-2	Pittsburgh No. 8	Ohio	505	22	0.4	1.4	3.7	94.5
11089	Allegheny Group coals	Pennsylvania	491	24	0.8	3.1	8.8	87.3
7265	Illinois No. 6	Illinois	641	20	0.2	0.5	1.4	97.9
6145	Lower Freeport	Pennsylvania	513	26	0.3	1.2	3.5	95.0

1/ Fifty percent of the weight of pyrite is smaller or larger than the diameter shown.
2/ Fifty percent of the pyrite grains have diameters smaller (or larger) than the diameter shown.

Calculated responses:
Btu recovery
Sulfur-to-Btu ratio
Btu/SO_2 index (B_I)

The range of the Btu/SO_2 Index (B_I) for the Lower Freeport No. 6A, Ohio, HRI 11986-1, coal is from 15.6, the value for the feed coal, to 69.2, the theoretical maximum B_I value attained by 100% pyrite removal with no loss of Btu from loss of any organic material. The results of the factorial experiment appear in Table 8.

The effect of the carbonyl treatment variables within the ranges tested on the amount and quality of the coal are given in Table 9.

An analysis of the experimental data shows the direction of a "best path" for further experimental study. The path followed, along which the Btu/SO_2 Index is increased, requires an additional 9.2 pounds of iron carbonyl/ton feed for every five-degree decrease in process temperature. This path was followed, starting at 170°C and 25 pounds $Fe(CO)_5$/ton coal. This starting point was the base level for temperature and dosage, which were the most significant factors in the fractional factorial design experiment. Steam treated coal was used as feed to the carbonyl reactor since steam pretreatment improved the Btu/SO_2 Index. Treatment time was held at 60 minutes rather than 30 minutes since this longer time improved the index slightly. The experimental conditions and analytical data for these "best path" tests are given in Table 10. Figure 5 shows how the "best path" experiment leads the B_I value to a maximum and pyritic sulfur to a minimum.

Table 8

Clean Coal Analyses Resulting from Various Combinations of Pretreatment and the Carbonyl Treatment Variables Time, Temperature, and Amount of Steam

(Lower Freeport No. 6A, Ohio, HRI 11986-1)

Pretreatment	Time, min	Temperature, °C	lb $Fe(CO)_5$/ ton Feed Coal	Yield of Clean Coal, Weight %	Clean Coal Analytical Values				lb SO_2/ 10^6 Btu	Btu Recovery, %	Btu/SO_2 Index (B_I) 3/
					Ash, %	Total Sulfur, %	Pyritic Sulfur, %	Calculated Btu/lb			
No	30	150	10	85.3	26.2	2.39	1.66	10,656	4.48	97.5	21.8
No	30	190	40	69.2	15.3	2.22	1.42	12,433	3.57	92.3	25.9
No	60	150	40	60.9	9.9	1.69	0.88	13,327	2.53	87.1	34.4
No	60	190	10	91.4	30.2	3.02	2.41	9,983	6.04	97.9	16.2
Yes	30	150	40	85.8 1/ 88.3	29.1 30.3	1.54 1.50	0.89 0.88	10,211 10,016	3.01 2.99	94.0 94.9	31.2 31.7
Yes	30	190	10	86.2	27.3	2.72	2.05	10,465	5.19	96.8	18.7
Yes	60	150	10	93.2	33.2	2.12	1.42	9,528	4.45	95.3	21.4
Yes	60	190	40	65.1	12.4	1.94	1.10	12,914	3.00	90.2	30.1
Feed	-	-	-	100.0	34.3	2.98	2.32	9,321	6.39	100.0	15.6

1/ Duplicated to evaluate equipment change.

2/ Calculated from Btu = 14961.8 - 162.3 (% ash) - 32.2 (% pyritic sulfur).

3/ B_I = (% Btu recovery)/(lb $SO_2/10^6$ Btu).

Table 9

The Primary Effects Within the Range Tested of Pretreatment and the Carbonyl Treatment Variables Temperature, Time, and Amount of Iron Carbonyl on the Clean Coal

(Lower Freeport No. 6A, Ohio, HRI 11986-1)

	Desired	Undesired
Increasing the Amount of $Fe(CO)_5$ Affects the Clean Coal		
Yield, weight percent		Decreases
Ash percent	Decreases	
Pyritic sulfur	Decreases	
Sulfur-to-Btu ratio	Decreases	
Btu recovery		Decreases
Btu/SO_2 index	Increases	
Decreasing Temperature (Carbonyl Treatment) Affects the Clean Coal		
Pyritic sulfur	Decreases	
Sulfur-to-Btu ratio	Decreases	
Btu/SO_2 index	Increases	
Increasing Time (Carbonyl Treatment) Affects the Clean Coal		
Btu recovery		Decreases
Btu/SO_2 index	Increases	
Pretreating the Coal Affects the Clean Coal		
Pyritic sulfur	Decreases	
Sulfur-to-Btu ratio	Decreases	
Btu/SO_2 index	Increases	

Table 10

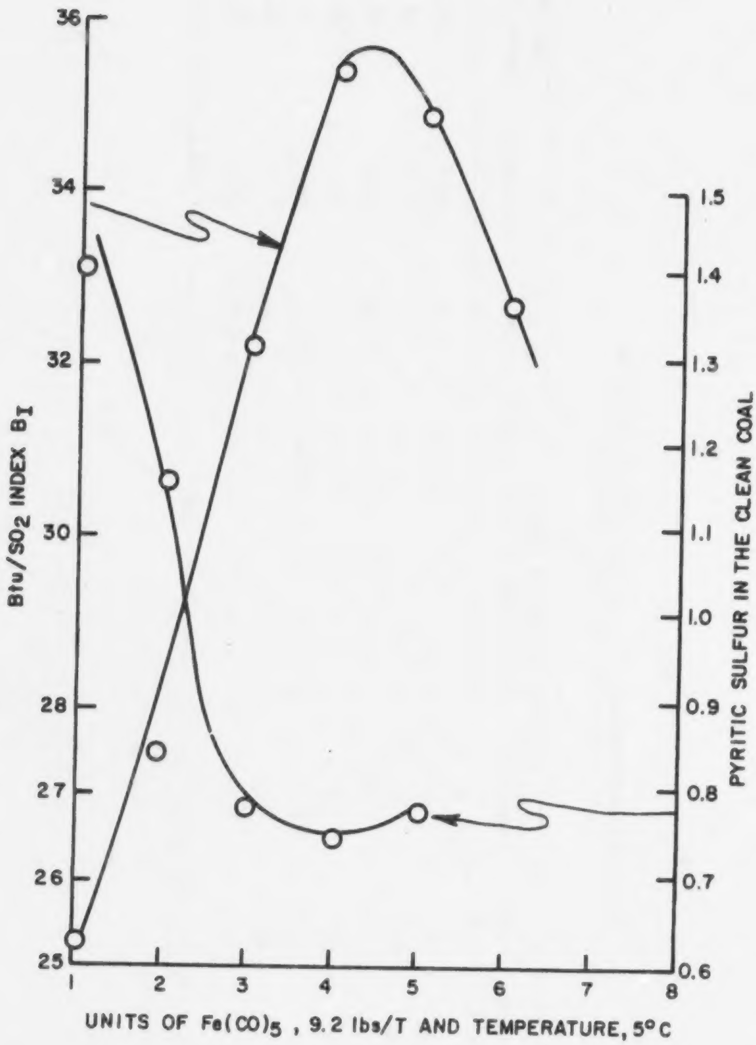
"Best Path" Experiment for Optimization of Magnex Response

(Lower Freeport No. 6A, Ohio, HRI 11986-1)

Temperature, °C	lb $Fe(CO)_5$/ ton Feed Coal	Yield of Clean Coal, Weight %	Clean Coal Analytical Values				lb SO_2/ 10^6 Btu	Btu Recovery, %	Btu/SO_2 Index (B_I) 2/
			Ash, %	Total Sulfur, %	Pyritic Sulfur, %	Calculated 1/ Btu/lb			
170	25	80.0	23.7	2.08	1.41	11,070	3.75	95.0	25.3
165	34.2	80.4	23.9	1.92	1.17	11,045	3.47	95.3	27.5
160	43.4	86.1	29.1	1.50	0.77	10,214	2.93	94.3	32.2
155	52.6	82.9	25.6	1.46	0.78	10,782	2.71	95.9	35.4
150	61.8	86.8	28.9	1.40	0.75	10,248	2.73	95.4	34.9
140	80.2	89.5	31.7	1.41	0.78	9,792	2.88	94.0	32.6
Feed	-	100.0	34.3	2.98	2.32	9,321	6.39	100.0	15.6

1/ Calculated from Btu = 14961.8 - 162.3 (% ash) - 32.2 (% pyritic sulfur).

2/ B_I = (% Btu recovery)/(lb SO_2/10^6 Btu).



CHANGE IN Btu/SO_2 INDEX (B_I) AND PYRITIC SULFUR IN THE CLEAN COAL BY FOLLOWING THE BEST PATH. (LOWER FREEPORT No. 6A, OHIO, HRI 11986-1) (IRON CARBONYL INCREASED 9.2 lbs/TON FOR EACH 5°C TEMPERATURE RISE)

FIGURE 5

STEAM PRETREATMENT

For the pretreatment, the variables time, temperature, and the steam atmosphere need to be fixed in order that the subsequent steps in the Magnex process will yield the desired result. The effect of temperature and amount of steam were tested in a partially replicated factorial design experiment, 3^2. Time of pretreatment was set at one hour, an arbitrary setting based upon previous work. The data generated by the experiment appear in Table 11. The conditions employed for the carbonyl treatment were the same as those used in the "best path" experiment which gave the best result. The responses evaluated were the same as those considered in the carbonyl treatment evaluation.

Within the limits tested, the effect of the steam pretreatment variables on the amount and quality of the clean coal are summarized in Table 12. It is speculated that the advantages brought about by steam pretreatment are due to a reduction in the low temperature volatiles and, based on work not reported in this paper, the small amount of elemental sulfur present in the feed coals.

A comparison between sink-float results and the beneficiation obtained by Magnex is plotted in Figure 6. Three Magnex results are plotted. The first is the preliminary amenability; the second is the result of studying the variables affecting carbonyl treatment, the best path results; the third builds upon the second but is enhanced by the results of studying the variables of pretreatment.

Table 11

Clean Coal Analyses Resulting from Various Combinations of Temperature and Steam During Pretreatment

(Lower Freeport No. 6A, Ohio, HRI 11986-1)

Temperature, °C	Steam, lb/ton	Product	Yield of Clean Coal Weight %	Clean Coal Analytical Values				lb SO2/ 10^6 Btu	Btu Recovery, %	Btu/SO2 2/ Index, (B_I)
				Ash, %	Total Sulfur, %	Pyritic Sulfur 1/ %	Calculated Btu/lb			
170	90	Cleaned Coal	75.6	22.4	1.36	0.74	11,303	2.40	91.7	38.2
170	252	Cleaned coal	80.9	24.5	1.39	0.76	10,961	2.53	95.1	37.6
170	426	Cleaned coal	74.5	18.4	1.39	0.69	11,953	2.32	95.5	41.2
200	90	Cleaned coal	87.9	29.5	1.44	0.82	10,148	2.84	95.7	33.7
200	90	Cleaned coal	84.9	27.6	1.29	0.69	10,460	2.46	95.3	38.7
200	252	Cleaned coal	86.7	30.3	1.27	0.68	10,023	2.53	93.2	36.8
200	252	Cleaned coal	87.8	31.0	1.31	0.77	9,906	2.54	93.3	35.3
200	426	Cleaned coal	84.9	27.5	1.35	0.71	10,476	2.57	95.4	37.1
230	90	Cleaned coal	90.6	34.8	1.33	0.75	9,290	2.85	90.3	31.6
230	252	Cleaned coal	91.4	29.9	1.33	0.76	10,085	2.63	98.9	37.6
230	426	Cleaned coal	90.6	32.2	1.31	0.75	9,712	2.69	94.4	35.1
230	426	Cleaned coal	91.1	33.5	1.32	0.79	9,500	2.78	92.8	33.4
Feed	-	-	-	34.3	2.98	2.32	9,321	6.39	100.0	15.6

1/ Calculated from Btu = 14961.8 - 162.3 x % ash - 32.2 x % pyritic sulfur.

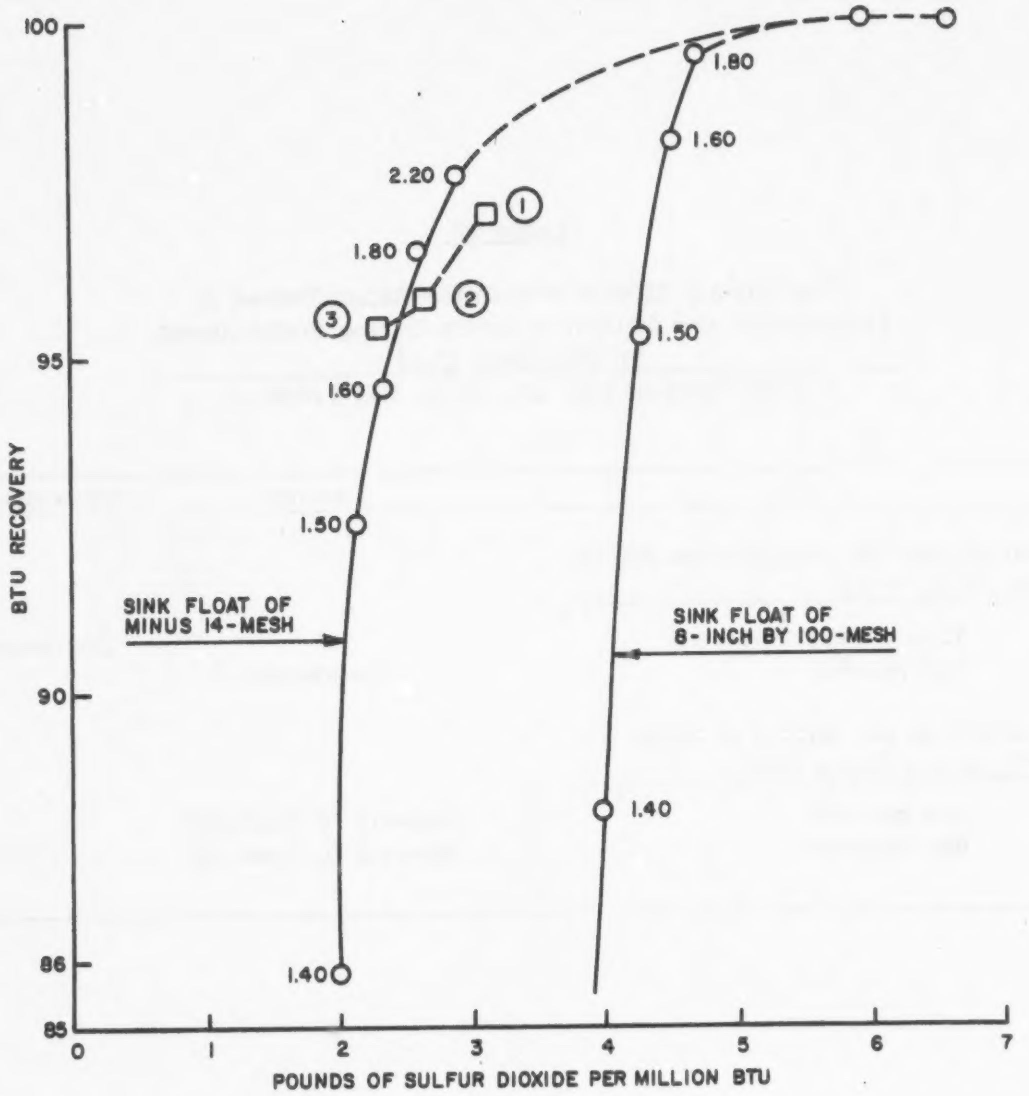
2/ B_I = (% Btu recovery)/(lb SO_2 per 10^6 Btu).

Table 12

The Primary Effects Within the Range Tested of Temperature and Amount of Steam During Pretreatment on the Clean Coal

(Lower Freeport No. 6A, Ohio, HRI 11986-1)

	Desired	Undesired
Decreasing the Temperature Affects the Clean Coal		
Yield, weight percent		Decreases
Ash percent	Decreases	
Increasing the Amount of Steam Affects the Clean Coal		
Ash percent	Appears to decrease	
Btu recovery	Appears to increase	



① FIRST MAGNEX AMENABILITY TEST

② CARBONYL TREATMENT VARIABLES OPTIMIZED

③ STEAM PRETREATMENT VARIABLES OPTIMIZED
(NUMBERS BY POINTS ARE SPECIFIC GRAVITIES)

COMPARISON OF MAGNEX AND SINK FLOAT
FOR BTU RECOVERY AND SULFUR EMISSION

FIGURE 6

CONCLUSIONS

The Magnex process is a novel dry method for cleaning fine coal which is projected to be cost competitive with existing processes. The Magnex technology possesses a considerable advantage over most existing processes. That advantage is the ability to make a coal-refuse separation by increasing the magnetic character of the refuse components of the raw coal but not the coal itself; this selectivity is contrasted to having to "live with" the existing distribution of whatever property is used for making the separation. At the present state of Magnex technology that advantage is best reflected in the considerable selectivity of the process for pyrite, and it is likely that advantage can best be exploited in conjunction with conventional coal preparation technology.

This paper has discussed two aspects of the ongoing commercialization effort -- (1) the effect of feed properties and (2) the effect of process variables on the Magnex process. An understanding of the interaction between feed characteristics and the process can lead to selection of preferred feed coals, to a better understanding of the process mechanism, and to process improvements. Regarding the effect of process variables, pyrite size consist data were given; for one (typical) coal the weight mean diameter was 556 microns. Also shown for this same coal was the way pretreatment variables and carbonyl treatment variables could be adjusted to produce a clean coal with a higher Btu recovery and lower sulfur-to-Btu ratio than could be achieved with a perfect sink-float separation. This illustrates how an understanding of the relationship between process variables and the effectiveness of the separation leads to process optimization.

A coal beneficiation process which is cost effective and produces a sharp separation requires a thorough understanding of the interactions between the coal characteristics and the process, and the relationship between process variables and the cleaning efficiency. It is through the studies described in this paper and the ongoing effort that this understanding is being won.

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PANEL DISCUSSION

PANEL DISCUSSION ON
PROPSECTS FOR CHARACTERIZATION AND REMOVAL OF ORGANIC SULFUR FROM COAL

Preliminary Comments

by
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Until about 1970, little interest was shown in characterizing the organic sulfur in coal, and even less in removing it. In earlier work done in numerous research laboratories throughout the world, sulfur analyses were not routinely carried out or reported on products resulting from reactions performed on coal. Coal liquefaction products seldom had sulfur contents reported, and though someone must have determined the sulfur content of coal acids obtained by air oxidation, I could not find such data when I started looking for it. Here I must admit that this data was not available even in our own laboratory. With such indifference about coal sulfur content, it is no wonder that we know so little about it. We do not even have a satisfactory procedure for determining organic sulfur in coal, although several methods are being explored. These include such techniques as X-ray fluorescence and low-temperature ashing. The lack of a reliable, direct determination of organic sulfur in coal is particularly annoying in the case of treated coal, especially desulfurized coal. In these samples, anomalous organic sulfur values are obtained because of apparent errors in the determination of the other sulfur forms. This may lead to erroneous conclusions. Hopefully, the aforementioned new methods for organic sulfur determinations will be developed to the point where they can be applied satisfactorily to treated coals.

Characterization of the organic sulfur by functional group is an equally challenging problem. Repeated attempts to determine thiol and alkyl thioether groups in coal by classical methods have led to inconclusive results and there is no good evidence to either accept or reject their presence. Undoubtedly, both such groups exist in coal, but as yet there is no good procedure for their determination.

Current evidence from hydrogenation studies, oxidative desulfurization, and alkaline extraction does point to two types of organic sulfur in coal. Roughly half the organic sulfur is amenable to removal by these methods, indicating its presence in some types of structures which are rather easily desulfurized, e.g., thiols, linear thioethers. The remainder of the organic sulfur appears to resist these treatments, although it can be removed by treatment that cleaves such sulfur compounds as dibenzothiophene. Hence, it is supposed that much of the organosulfur in coal is in such thiophenic structures. Though chemistry is known which can remove sulfur from these structures, it tends to be drastic. Hydrogenation, for example, does accomplish this, but only by adding sufficient hydrogen to liquefy the coal. Oxidation, followed by basic hydrolysis at elevated temperature, can effectively remove sulfur from dibenzothiophene without further change. In the laboratory, using alkali metals as reductants, it has been possible to bring total sulfur levels down to 0.1 percent.

Two principle types of reaction have been used for removal of organic sulfur - degradative extraction with base (NaOH) at elevated temperature and oxidation with concurrent or subsequent hydrolysis. The oxidants which we have heard about are air or oxygen, nitrogen oxides, and chlorine. Peroxygen compounds have also been used. As yet, we know little about the chemistry of some of these desulfurization reactions, since little model compound work has been done on reactions of this type. It is planned to carry out such studies in the immediate future.

All of the methods utilized so far have one thing in common. The maximum amount of organic sulfur removed is between 40 and 60 percent, depending on the coal and reaction conditions. This seems to be the limit approached by the several methods. As I noted previously, this could be the result of two types of organic sulfur, one of which behaves chemically like dibenzothiophenic sulfur and resists most chemical treatment. If this is true, it may not be possible to remove all of the organic sulfur by simple chemical means.

The prospects for characterization of the organic sulfur in coal appear good, at least in terms of total organic sulfur and some functional groups. Practical methods for removal of up to half of the organic sulfur are at the stage where process development can be undertaken provided environmental acceptance of the product can be guaranteed. Consumer demand for such a product already exists. Even for those coals where chemical desulfurization does not provide a product with totally acceptable sulfur content, the partial reduction might allow the coal to be mixed with a coal of lower sulfur content. In other situations, the treated coal can be used to lessen the burden placed on the coal consumer who operates sulfur reducing equipment, such as a flue gas desulfurization facility. In summary, the prospects are good if there is encouragement to proceed.

PANEL DISCUSSION ON THE USE OF MODEL ORGANOSULFUR COMPOUNDS TO INVESTIGATE THE EFFECTIVENESS OF OXYDESULFURIZATION OF COAL

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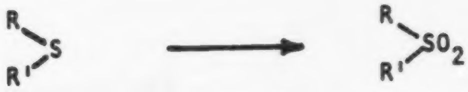
Ames, Iowa

Although some progress has been made in determining the nature of organosulfur components in coal, there is still very little information detailing the identity or even the functional group distribution of these sulfur moieties. Specific organosulfur compounds such as thiophenes and dibenzothiophenes have been isolated from coal and identified. Typically, these materials were identified as an incidental consequence of investigating other types of compounds in coal. Efforts have also been made to delineate the organosulfur functional group distribution through chemical and physical properties. The chemical and physical bases for these studies were, at best, obscure and the results were, in most cases, inconclusive. Investigations are underway in this laboratory and at other locations to detect organosulfur species directly by using such techniques as ^{33}S NMR and ESCA. However, none of these efforts have unambiguously established the organosulfur functional group distribution in coal.

During the initial phases of this investigation, it has been our approach that a definitive knowledge of the organosulfur functional group distribution is not a prerequisite for investigating the viability of various desulfurization schemes. Thus to evaluate a specific desulfurization process, it is sufficient to measure the propensity of a representative spectrum of organosulfur model compounds toward desulfurization under the specific process conditions.

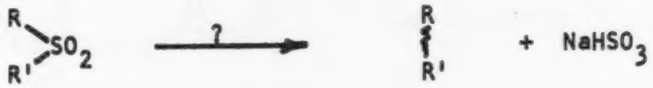
Although our conclusions necessarily extend to other oxydesulfurization processes, the basis for our initial investigations has been the Ames version of the oxydesulfurization process. Conceptually, oxydesulfurization is a two-step process and can be described by the following chemical equations:

Step 1. Oxidation



Reaction Conditions: 150°C, 200 psi O_2, 0.2 M aq. Na_2CO_3, 1 hour.

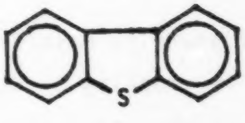
Step 2. Desulfurization



While there is some precedent in the literature for the oxidation of sulfides by molecular oxygen, the basis for Step 2 occurring under these reaction conditions is rather tenuous. Furthermore it is important to realize that the sulfur is not extruded from the organosulfur moiety until the second step. Thus, complete conversion of the organic sulfide in Step 1 does not constitute desulfurization.

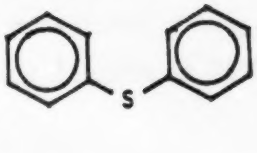
The following organosulfur compounds have been subjected to Ames process conditions (150°C, 200 psi O_2, 0.2 M aqueous Na_2CO_3, 1 hour) to afford the results indicated.

1.



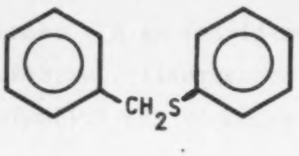
95% Recovery of starting material

2.



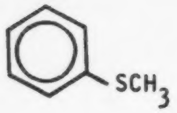
98% (63%*) Recovery of starting material

3.



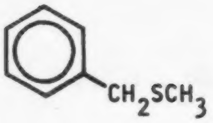
89% Recovery of s
starting material

4.



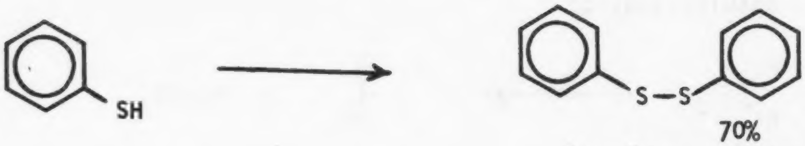
90% (54%*) Recovery
of starting material

5.



82% Recovery of
starting material

6.



70%
No other products detected.

* 25 grams raw coal added

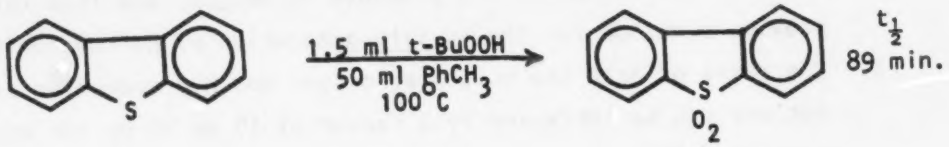
In each of the first five cases, no oxidation products were detected.

While these are preliminary results and we are still refining our experimental techniques, we are reasonably certain that the first five compounds do not react under Ames conditions, even in the presence of raw coal. We believe that the reduced recoveries of starting material in the presence of raw coal (results 2 and 4) reflect adsorption of the organosulfur into the microporous surface of the coal and mechanical loss associated with working up the reaction mixture. We are in the process of modifying our experimental technique to obviate these analytical problems.

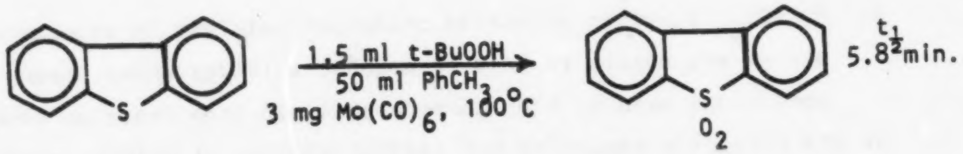
In the case of thiophenol (result 6), 70% of the starting material can be accounted for as the simple disulfidic oxidative coupling product. Although we have not accounted for the remaining 30% of the starting material, the initial product of the reaction, diphenyl disulfide, appears to be stable under Ames process conditions and is not efficiently oxidized to benzene sulfonic acid. Therefore it is our preliminary conclusion that, under oxydesulfurization process conditions, most if not all organosulfur compounds are unreactive!

Another of our primary initial objectives was to develop catalysts and reaction conditions for the efficient conversion of organic sulfides to the oxidized product (Step 1 of the Ames process) using moderate temperatures and atmospheric pressure. Thus far, we have been able to efficiently oxidize dibenzothiophene, phenyl sulfide, and diphenyl disulfide under the following conditions.

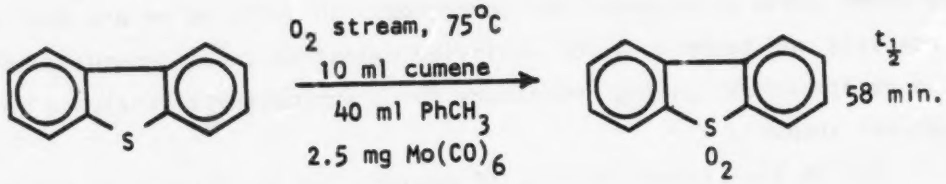
1.



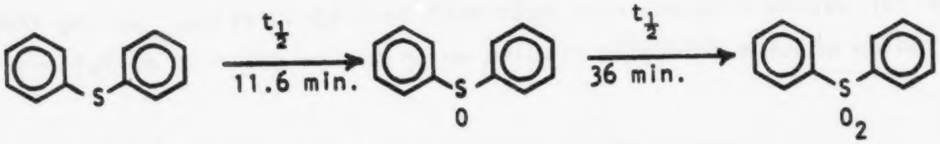
2.



3.

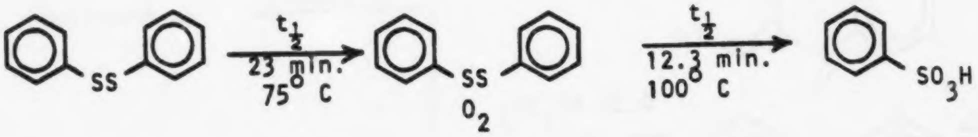


4.



Reaction Conditions: 3.1 ml t-BuOOH, 50 ml $PhCH_3$, 6 mg $Mo(CO)_6$, 75°C

5.



Reaction Conditions: 13 ml t-BuOOH, 50 ml $PhCH_3$, 12 mg $Mo(CO)_6$

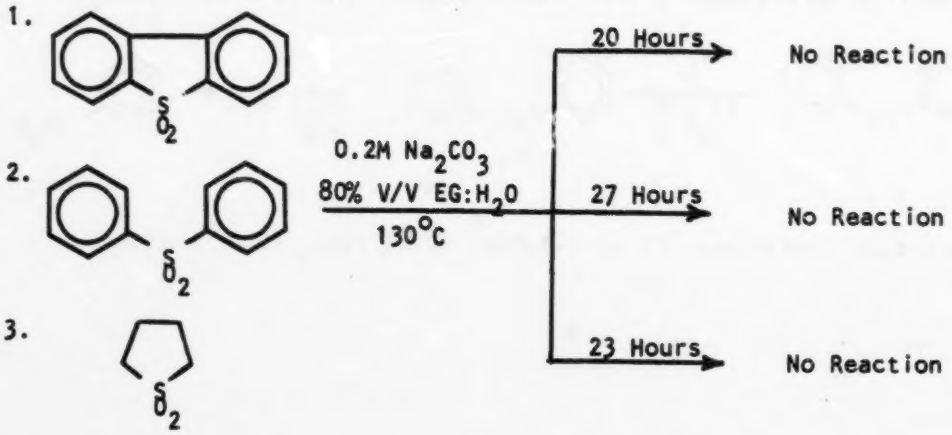
On the basis of our experiments, we have reached the following conclusions.

1. Organic sulfides can be effectively oxidized to the sulfones by alkyl hydroperoxides in organic solvents.
2. In the absence of added hydroperoxide, these same sulfides can be oxidized just as effectively by bubbling a stream of oxygen through the organic solvent provided a substance such as cumene or tetralin is present. These substances are known to readily form hydroperoxides in the presence of oxygen, and thus they provide a method for the *in situ* generation of hydroperoxides.
3. The rates of both the molecular oxygen and hydroperoxide oxidations can be increased by a factor of 10 to 15 by the addition of $Mo(CO)_6$.
4. $Mo(CO)_6$ is not an effective oxidation catalyst in aqueous media and we are unable to oxidize organic sulfides under aqueous conditions even at high temperatures and long reaction times.

We are presently expanding our initial studies of $Mo(CO)_6$ catalysis to other types of organosulfur compounds. In addition we are evaluating catalysts and techniques for achieving oxidation under aqueous conditions, and we are investigating techniques for grafting these catalysts to a polymer support.

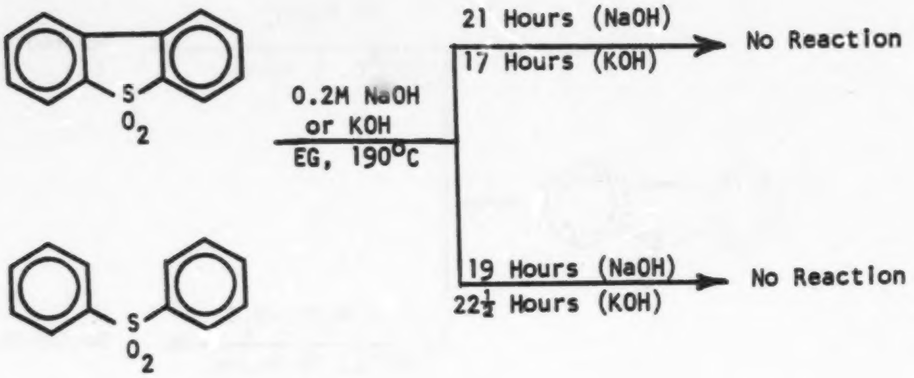
Our initial investigations of desulfurization (Step 2 of the oxydesulfurization process) have been much less encouraging. During these studies we have generated results which can be outlined as follows:

DESULFONATION REACTIONS OF MODEL COMPOUNDS

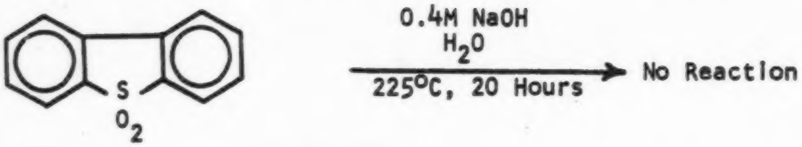


4.

5.


S
O_2
0.2M NaOH
or KOH
EG, 190°C
21 Hours (NaOH)
17 Hours (KOH)
No Reaction
S
O_2
19 Hours (NaOH)
22½ Hours (KOH)
No Reaction

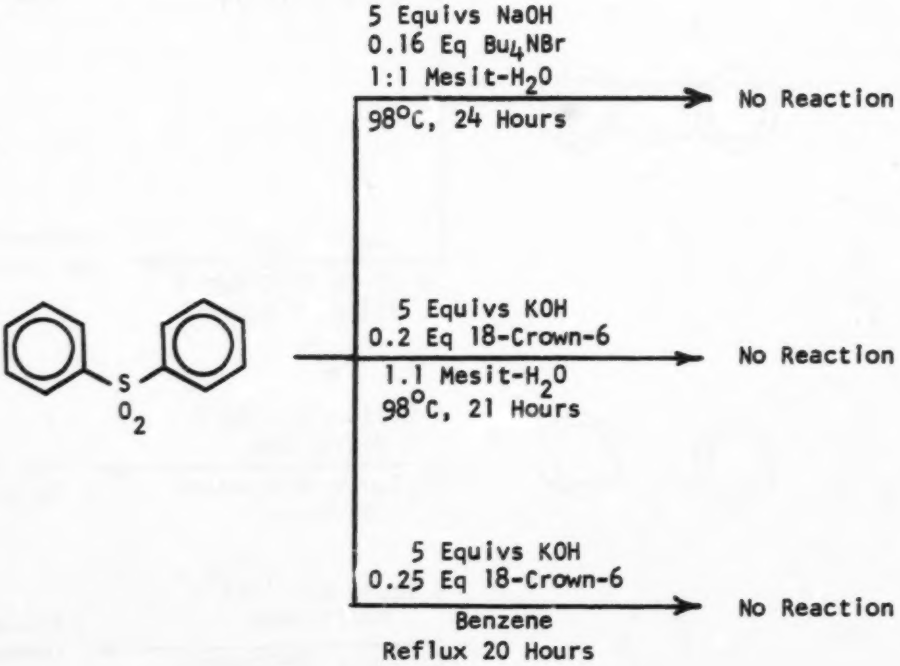
6.


S
O_2
0.4M NaOH
H_2O
225°C, 20 Hours
No Reaction

7.

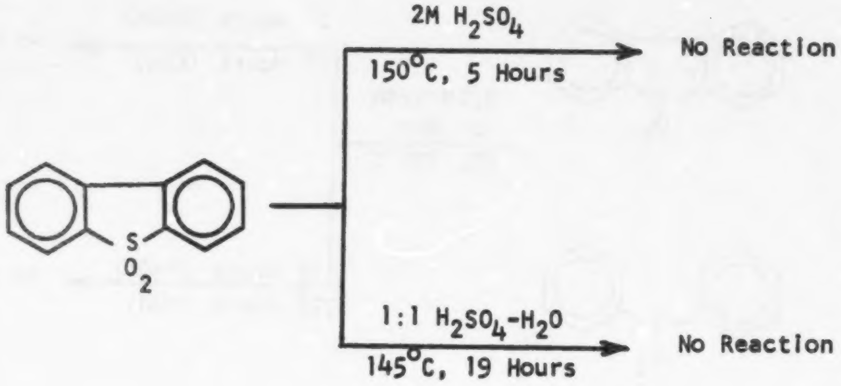
8.

9.


5 Equivs NaOH
0.16 Eq Bu_4NBr
1:1 Mesit-H_2O
98°C, 24 Hours
No Reaction
S
O_2
5 Equivs KOH
0.2 Eq 18-Crown-6
1.1 Mesit-H_2O
98°C, 21 Hours
No Reaction
5 Equivs KOH
0.25 Eq 18-Crown-6
Benzene
Reflux 20 Hours
No Reaction

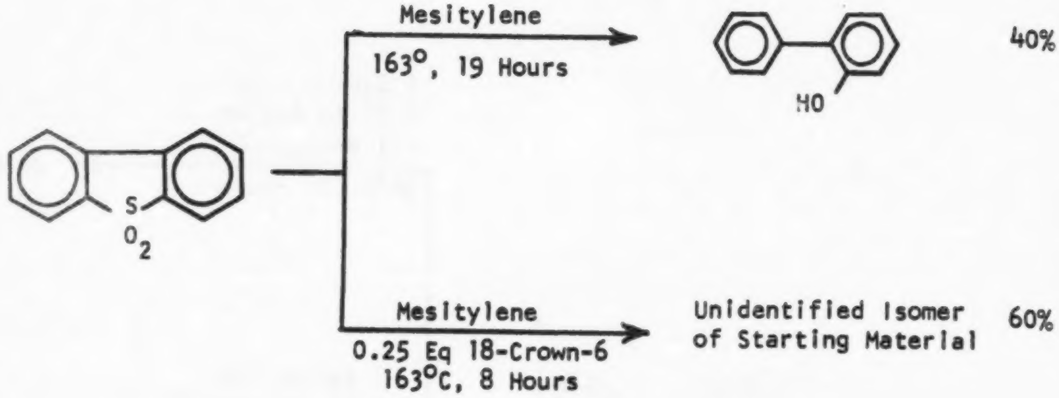
10.

11.

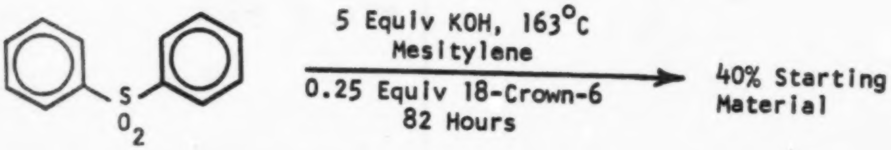


12.

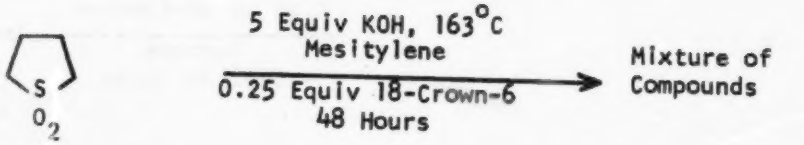
13.



14.



15.



Reactions 1-6 represent increasingly rigorous reaction conditions in an attempt to achieve desulfurization while working within the scope of the Ames process. Even at 225°C for 20 hours, no reaction had occurred. Reactions 7-9 represent attempts to facilitate the reaction through the use of phase transfer reagents. This unsuccessful approach was based on the premise that a homogeneous reaction will proceed more rapidly than a heterogeneous reaction. On the basis of reactions 10 and 11, it appears that the reaction cannot be effected in strong acid media either. Reactions 12-15 represent the only partially successful attempts at desulfonation. It appears that the rate of the reaction can be substantially increased by solublizing the KOH with crown ether. However, even under these reaction conditions, the rates are very slow; and these conditions do not represent a viable method for desulfonation. Presently we are studying the effects of higher temperatures and catalysts on this reaction.

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